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Nitrosamine Analysis of Diesel Crankcase Emissions

New England Inst. for Life Sciences
Waltham, MA

Prepared for

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16. ABSTRACT

The main objective of this work was to qualify and employ artifact-free methods in the testing of crankcase emissions of heavy-duty diesel engines for volatile N-nitrosamines. As we worked toward the achievement of the main objective of this work, we also attempted to establish the sources of the crankcase emission nitrosamines. We examined the lubricating oils and the diesel fuels. As we gathered more information, new objectives were set. As a second objective, a survey of nitrosamine levels in unused and used oils was set. As a third objective a relationship between the nitrosability of the oils and the engine crankcase nitrosamine levels was sought so that nitrosamine levels could be predicted based on nitrosamine formations from the unused oils in tests conducted in the laboratory.

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Report No. TE450-259-81

Final Report

NITROSAMINE ANALYSIS OF DIESEL CRANKCASE EMISSIONS

Contract No. 68-03-2719

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FOREWORD

This report covers EPA contract no. 68-03-2719 conducted for the Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, MI 48105. The EPA project officer was Mr. Thomas M. Baines. The principal investigator for New England Institute for Life Sciences was Dr. David H. Fine and Laboratory Manager was Ms. Ulku Goff who was assisted by Mr. James Coombs. The project was performed during the period of September 11, 1978 through December 12, 1979.

I. INTRODUCTION

Amine type compounds are often present in lubricating oil as friction modifiers, metal deactivators, dispersants and corrosion and rust inhibitors (Schilling, G.J., Bright, G.S. 1977). Oxides of nitrogen (NO_x) are generated _in situ_ during the combustion process in the combustion chamber. Because N-nitrosation of amines _via_ oxides of nitrogen has been shown to be rapid, especially in nonaqueous solvents (Challis, B.C. _et al._, 1978), nitrosamines are to be considered likely contaminants in diesel crankcase emissions.

Challis _et al._, (1978) reported rapid formation of N-nitrosamines by gaseous oxides of nitrogen (N_2O_3, N_2O_4) in organic solvents. Both N_2O_3 and N_2O_4 are used as nitrosating agents for the synthesis of N-nitrosamide in organic solvents (White, E.H., 1955). Formation of N-nitrosamines in cigarette smoke from dinitrogentrioxide (N_2O_3) has been demonstrated by Neurath _et al._, (1976) and Spincer and Westcott (1976).

Keefer _et al._, (1976) observed that relatively small amounts of metal salts catalyze the nitrosation action of nitric oxide (NO) in organic solvents. Challis _et al._, (1978) have observed the catalytic effects of metal salts such as ZnI_2, $ZnBr_2$, $CuCl_2$, $Fe(NO_3)_3$, $AgNO_3$ and $CuSo_4$ for NO nitrosation reaction. They also found that the metal salt catalyzed reactions in organic solvents were substantially faster than N-nitrosamine formation by acidified nitrite (Challis, B.C., and Outram, J.R. 1978).

Zinc dithiophosphate is added into automotive lubricating oils, (Schilling, G.J. and Bright, G.S. 1977) to reduce friction between metal parts, decrease wear and prevent corrosion and rusting of metal parts that are in contact with the lubricant. The salt also retards the oxidative decomposition of the oil (Schilling, G.J. and Bright, G.S., 1977). A catalytic effect of this salt might be expected during NO nitrosation of amines in the oils.

Although NDMA has not been observed to be present in automobile exhaust, it has been detected in Colorado's Eisenhower road tunnel (Hare, C.T. Montalvo, D.A., 1977a). Gordon's work has indicated the presence of highest levels of NDMA on the grounds of the Los Angeles County-University of Southern California Medical Center which is located near the Golden State Interchange and San Bernadina Freeways and is also close to the local traffic (Gordon, R.J, 1978). This has suggested a relationship with the vehicle emissions and the NDMA levels. Cadle, S.H. and Mulawa, P.A. concluded that the exhaust emissions of amines from current-production automobiles cannot account for nitrosamine levels measured in the Eisenhower Tunnel in Colorado and on Cross-Bronx Expressway in New York City (Cadle, S.H., Mulawa, PA, 1980). Previous research on diesel engine crankcase emissions as a source of nitrosamine emissions has been inconclusive. In a recent study, NDMA was detected using a gas chromatograph (GC) interfaced to a nitrogen selective Hall detector; confirmation of the finding by GC-mass spectrometry (MS) was complicated by co-eluting compounds (Hare, C.T., Montalvo, D.A., 1977b). An analysis of diesel crankcase emissions contained in Tedlar bags did not indicate that NDMA was present (Hare, C.T., Montalvo, D.A., 1977c.). When positive results were obtained, little effort was addressed to the possibility that the nitrosamines were being formed as analytical artifacts, either during trapping, or during analysis. A background on nitrosamines is given in appendix J.

II. SUMMARY

The main objective of this work was to qualify and employ artifact-free methods in the testing of crankcase emissions of heavy-duty diesel engines for volatile N-nitrosamines (See Appendix A for the scope of work). In order to achieve this objective the following tasks were performed.

TASK I. Sampling and Analysis Method Development and Qualification

This objective was achieved by developing a crankcase sampling method that involved trapping the volatile nitrosamines in either a pH 4 phosphate-citrate buffer solution or in a Thermosorb™/N Air Sampler, followed by extraction of the traps with appropriate solvents, concentration and analysis of the material on a gas chromatograph and/or high pressure liquid chromatograph interfaced to a TEA™ Analyzer.

Detection limits, based on a 60L sample, were 0.1 $\mu g/m^3$ for N-nitrosodimethylamine (NDMA) and 0.16 $\mu g/m^3$ for N-nitrosomorpholine NMOR. Validation of the reliability of the method included the intentional addition of both amines and/or nitrogen oxides. Confirmation of the identify of the nitrosamines was accomplished by high resolution mass spectrometry.

TASK II. Engine Selection

Test engine selection was made so that the influence of the engine type could be determined. For this reason a total of four engines, 3 heavy-duty (HD) and one light-duty (LD) were selected.

TASK III. Engine Testing

This objective was achieved by obtaining crankcase emission samples from the HD test engines during a 7-mode schedule and from the LD test engine during a 2-mode schedule and analyzing these samples for volatile nitrosamines by the methods described in TASK I. One of the engines selected was tested with four different types of lubrication oils to establish the influence of the oil type. The 7 modes used for heavy duty testing were modes 2, 4, 6, 7, 8, 10, 12 of the Federal 13 mode sequence. The light duty testing was performed at 20 and 50 mph.

All the samples obtained during engine testing contained NDMA at levels ranging from 0.2 $\mu g/m^3$ to 28 $\mu g/m^3$ and some samples contained NMOR at levels between 0.2 $\mu g/m^3$ and 2 $\mu g/m^3$.

As we worked toward the achievement of the main objective of this work, we also attempted to establish the sources of the crankcase emission nitrosamines. We examined the lubricating oils and the diesel fuels (see Appendix B). As we gathered more information, new objectives were set.

As a second objective, a survey of nitrosamine levels in unused, and used oils was set, for which the following tasks were carried out.

TASK IV. Oil Analysis Method Development

This task was performed by developing an oil analysis method that involved the transfer of volatile nitrosamines by bubbling air through the heated oil sample onto a ThermoSorb™/N Air Sampler, followed by elution of the sampler with acetone and analysis of the eluate on a gas chromatograph interfaced to a TEA. Detection Limits, based on 50 gm sample, varied from 0.1 part-per-billion (ppb) for NDMA to 1.0 ppb for N-nitrosodibutylamine (NDBA). Artifact experiments were carried out by intentional addition of amines into the oil samples and the ThermoSorb™/N Air Sampler for the validation of the method.

TASK V. Selection and the Survey of Oil Samples

This task was achieved by conducting:

a) A survey of the nitrosamine levels in unused oil samples to determine the effect of the oil type.

b) A survey of the used oil samples that had been obtained at progressive time intervals of usage, to determine the effect of the usage duration on the nitrosamine levels.

As a third objective, a relationship between the nitrosability of the oils and the engine crankcase nitrosamine levels was sought so that nitrosamine levels could be predicted based on nitrosamine formations from the unused oils in tests conducted in the laboratory.

To complete this objective the following tasks were conducted.

TASK VI. Oil Nitrosation Method Development

This objective was achieved by developing a method of nitrosation of the nitrosamine precursors in the oils which involved bubbling a NO/NO_2 gas mixture through the sample. The nitrosamines formed were picked up by the gas stream and collected on a ThermoSorb™/N Air Sampler which was then eluted with acetone and the eluate analyzed on a gas chromatograph interfaced to a TEA™.

TASK VII. Survey of the Nitrosability of the Oils

This test was performed by nitrosating unused and used oils samples that were acquired from oil and engine manufacturing companies. The nitrosated unused oils contained NDMA at levels from nondetectable to about 200 ppb and NMOR at levels between nondetectable and about 25 ppb.

III. EXPERIMENTAL

A. MATERIALS

Organic solvents (Distilled in Glass™) were obtained from Burdick and Jackson (Muskegon, MI). Morpholine (Reagent ACS), piperidine (practical), pyrrolidine (practical), dipropylamine (practical) were obtained from Eastman Kodak Company (Rochester, NY). Dimethylamine (40%), and L-Ascrobic Acid were obtained from Aldrich Chemical Company (Milwaukee, WI). Standard nitrosamine solutions and ThermoSorb™/N Air Samplers were obtained from the Analytical Services Laboratory of Thermo Electron (Waltham, MA).

The pH 4 phosphate-citrate buffer, sulfamic acid (certified), and sodium sulfate (anhydrous certified ACS) were obtained from Fisher Scientific Corp. (Fairlawn, NJ). Gas mixtures of $NO + NO_2$ prepared in nitrogen (N_2) were obtained from Scientific Gas Products (South Plainfield, NJ). DL-tocopherol was obtained from Chemalog (Chemical Dynamics Corp., South Plainfield, NJ). The GC packing material, 10% Carbowax 20M, 0.5% KOH on Chromosorb WHP 80/100, was obtained from Analabs, Inc. (North Haven, CT). The used and fresh oil samples were obtained from various U.S. oil and engine manufacturers.

B. APPARATUS

The gas chromatography (GC) analyses were carried out with a Thermo Electron GC-661 interfaced to a TEA™ (Thermo Electron Corp., Waltham, MA). The GC column was packed with 10% Carbowax 20M and 0.5% KOH on Chromosorb WHP, 80/100 in a 1/8" o.d. x 12' long stainless steel tube. NDMA analyses were carried out at 110°C; the other volatile nitrosamines were analyzed at 175°C. The high pressure liquid chromatograph (HPLC) analyses were carried out with a Varian 8500 LC pump (Varian Instrument Division, Palo Alto, CA) interfaced to a TEA™. The liquid chromatogrphy (LC) column was a porasil 10 (3.9 mm x 300 mm) (Waters Associates, Milford, MA), used with a solvent system that contained 4 to 8% acetone in isooctane. The LC injector was a model U6K (Waters Associates). Bendix Mesa C-116 air pumps (Bendix Corporation, Rochester, NY) were used for sample collection.

Air flow rates of the pumps were calibrated against a Hastings ALL 10 L mass flow meter (Teledyne Hastings-Raydist, Hampton, VA). The method development and validation for crankcase emission analyses were carried out using a Mack ENDT 676 engine located at Thermo Electron Corporation.

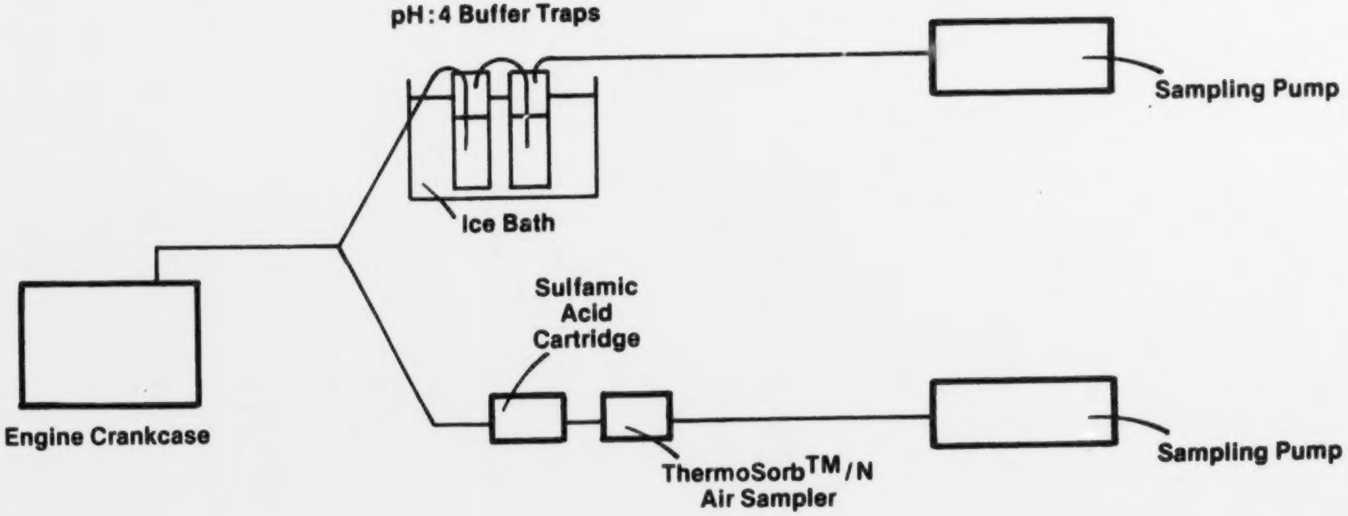
The nitrosamine measurements of crankcase emissions were made on Mack ETAY (B) 673A, Detroit Diesel 6V-71N, Caterpillar 3406, and a Mercedes Benz 240D which were operated by the Emissions Research Department of Southwest Research Institute (SWRI), San Antonio, TX.

C. PROCEDURES

TASK I. Sampling and Analysis Method Development and Qualification

Two trapping techniques were developed: dry traps consisting of a ThermoSorb™/N Air Sampler in series with a sulfamic acid cartridge, and a liquid trap consisting of a phosphate-citrate buffer at pH 4 in a glass impinger tube. Crankcase emissions from the engine were collected by means of a toggle valve (i.d. 1/4") or manual rotary valve (i.d. 1/4") situated on the breather pipe housing of the engine cover. Parallel sampling was done after splitting the teflon line a few inches from the valve by means of a plastic tubing connector (Pharmaseal Inc., Toa Alto, P.R.). The connector and the traps were connected by 1 to 2' of teflon tubing (o.d. 1/4", i.d. 1/8"). The sample collection apparatus is illustrated in Figure 1. Each HD engine was run through seven different 1/2 hour test modes during which engine speed and load were kept constant. Separate samples were collected during each mode at a flow rate of 2L/min.

(Descriptions of the heavy- and light-duty engines and the measurements of the engine speed, load, power, water and crankcase temperatures, crankcase NO and NO_2 concentration and flow rates in each test mode were provided by SWRI and are given in Appendix C.) Precise time and flow data were used to calculate sample throughput. After collection, the samples were stored in a dry ice box or freezer until the time of analysis.


pH:4 Buffer Traps
Ice Bath
Sampling Pump
Engine Crankcase
Sulfamic Acid Cartridge
ThermoSorb^{TM}/N Air Sampler
Sampling Pump

Sampling Time: 1/2 to 1 hr
Flow Rate: 2 L/min

Figure: 1 Sample Collection from Crankcase Emissions

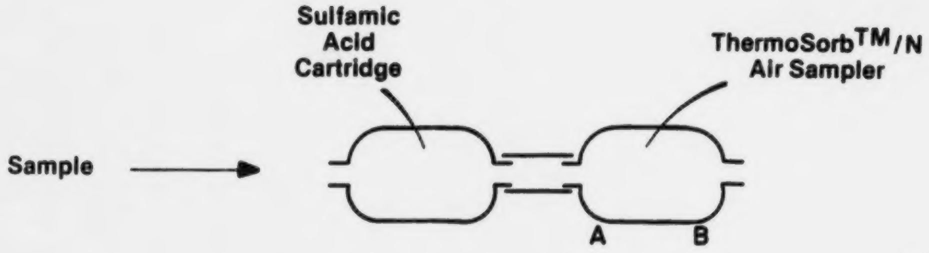
1. ThermoSorb™/N Air Sampler/Sulfamic Acid Cartridge

According to the supplier, ThermoSorb™/N Air Samplers were developed for artifact-free collection of N-nitrosamines from ambient air (Rounbehler, D.P. et al., 1980); for sampling air from diesel engine crankcase emissions, the relatively high nitrogen oxide (NO_x) levels necessitated placing a sulfamic acid cartridge in front of the ThermoSorb™/N Air Sampler. Sulfamic acid reacts with the incoming NO_x and amines, thus preventing possible artifactual nitrosation on the ThermoSorb™/N Air Sampler at high NO_x levels (Goff, U.G. and Coombs, J.R., 1979, unpublished work).

At the end of the sampling period the ThermoSorb™/N Air Sampler and sulfamic acid cartridges were removed and separated. The ThermoSorb™/N Air Sampler was washed to remove nonpolar oily materials by reverse eluting (See Figure 2) with 10 ml pentane followed by 2 ml of a mixture of dichloromethane and pentane (5/95). The cartridge was then dried by blowing carrier gas through it. The N-nitrosamines were finally eluted from the cartridge with 1.5 to 2.0 ml acetone. A 10 to 25 µl aliquot of the acetone fraction was introduced into the GC-TEA or HPLC-TEA.

2. Phosphate-Citrate pH 4 Buffer Traps

These traps consisted of two glass impingers (240 x 30 mm) in series, each containing 40 ml of a phosphate-citrate solution buffered at pH 4 together with 0.5 to 1 g sulfamic acid. The traps were immersed in an ice bath. The sulfamic acid was used because it inhibits nitrosation (Fan, T.Y. et al., 1977a) by competing with amines for the nitrosation agent. At the end of the sampling time the trap contents were transferred into separatory funnels and extracted with 2 x 10 ml pentane to remove the nonpolar oily materials from the aqueous phase. The pentane fraction was discarded. The trap contents were then extracted with 3 x 10 ml of dichloromethane (DCM), which extracted the nitrosamines. The DCM fraction was dried by passing the sample through a funnel containing 25


Sulfamic Acid Cartridge
ThermoSorb^{TM}/N Air Sampler
Sample
A
B

1. 10 ml Pentane wash from B to A.
2. 2 ml 5/95 Dichloromethane/Pentane wash from B to A.
3. Dry the cartridge by blowing carrier gas through it.
4. 1.5 - 2 ml Acetone wash from A to B.

Figure: 2 Extraction of Nitrosamines from ThermoSorb^{TM}/N Air Sampler sodium sulfate and then was concentrated in a Kuderna Danish evaporator to 1 ml. A 10 to 25 μl aliquot of the DCM concentrate was introduced into GC-TEA and/or HPLC-TEA for analysis.

ARTIFACT CONTROL EXPERIMENTS

A series of experiments were carried out to ensure that if nitrosamines were detected they were present in the engine crankcase emissions at the calculated amounts, and were not being formed during sampling and/or analysis.

1. Tests with Phosphate-Citrate Aqueous Traps

Recovery studies were carried out by adding 500 ng each of NDMA, N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosodibutylamine (NDBA), N-nitrosopiperidine (NPiP), N-nitrosopyrrolidine (NPYR) and N-nitrosomorpholine (NMOR) to the traps and passing 200 L of air through the traps at a flow rate of 2 L/min. The recovery efficiency for NDPA and NDBA was inadequate (see Table 1), and the liquid traps cannot be used for these two nitrosamines. For the two nitrosamines of interest, NDMA and NMOR, however, the recovery was 77 and 82%, respectively.

The overall efficiency of the aqueous buffered traps were tested by introducing 500 ng each of the mix of 7 nitrosamines into the incoming air stream prior to two traps in series. In all cases, 96% of the recovered nitrosamines were found in the first trap.

The possibility that nitrosamines could be formed artifactually during collection and/or analysis was tested both in the laboratory and during tests on a diesel engine. Dimethylamine (DMA), piperidine (PIP), pyrrolidine (PYR) and morpholine (MOR) were used as the test amines. DMA and MOR were selected because the nitrosamine derivatives of DMA and MOR were found to be present in crankcase emissions; piperidine and pyrrolidine were selected with the thought that they would make the artifact formation of nitrosamines more recognizable since NPiP and NPYR don't exist in the emissions.

Table 1
Extraction Efficiency of Various Nitrosamines (500 ng each) from pH 4 Phosphate-Citrate Buffer Traps (40 ml)

Nitrosamine	Recovery (%)*
NDMA	77
NDEA	66
NDPA**	9
NDBA**	N.D.
N-PiP	66
NPYR	88
NMOR	82

* The recovery is the average of two measurements.

** These nitrosamines were extracted into the pentane layer.

The laboratory simulation studies were carried out using the apparatus shown in Figure 3. Fifty μg of each amine was added to the traps and the NO and NO_2 concentration adjusted to 100 ppm and 7 ppm, respectively, by bleeding air into the lines. This concentration of NO_x is an approximation of the NO_x levels present in the crankcase emissions of the Mack 676 ENDT engine under actual operating conditions. Two measurements were performed; one with 1/2 hr sampling time, and the other with 1 hr sampling time. In each case the flow rate was 2.0 L/min, (6 mg NO + 0.4 mg NO_2 for 1/2 hr sampling; 12 mg NO + 0.8 mg NO_2 for 1 hr sampling). In every case, the nitrosamine derivative of the added amines could not be detected (sensitivity level per trap 0.006 μg NDMA, 0.018 μg/ NPiP, NPYR and NMOR).

The artifact studies during engine operation were carried out using the Mack 676 ENDT engine, using typical operating conditions. At the time, the NDMA level in the crankcase blowby was 0.1 μg/m^3. Four experiments were conducted (see Table 2). In the first, 50 μg of MOR was added to the trap - NMOR was not found in the trap. Second, 50 μg of PYR was added to the trap - NPYR was not found in the trap. Third, using identical parallel traps, 50 μg, of DMA was added to one of the traps - no enhancement of the NDMA level was found when compared to the control trap. Fourth, using identical parallel traps, 63 μg of PYR was added to both traps. One of the parallel traps received an additional 14 mg of NO + 1 mg NO_2 (100 ppm NO and 7 ppm NO_2 in the gas stream). Neither of the two traps contained enhanced levels of NDMA, or detectable levels of NPYR.

The Teflon tubing connecting the crankcase to the traps was checked for the artifactual formation of nitrosamines. During engine sampling two liquid traps

(contin. on p. III-31)

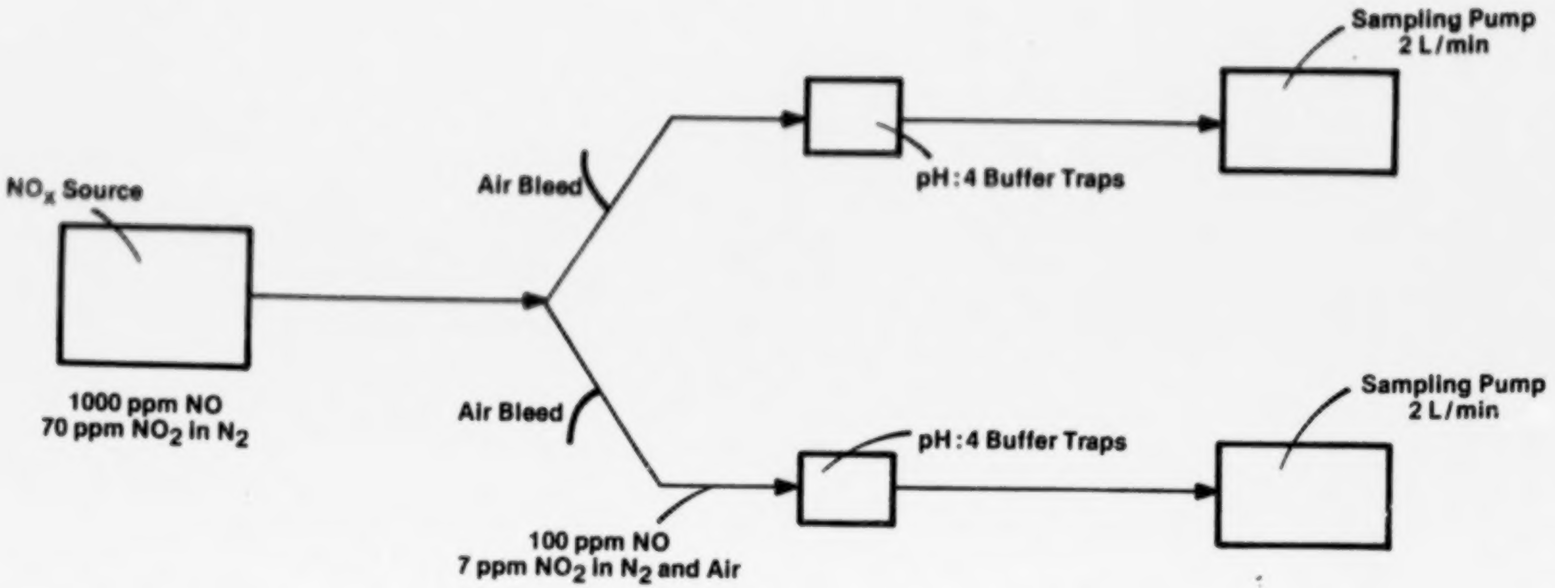

NO_x Source
1000 ppm NO
70 ppm NO_2 in N_2
Air Bleed
Air Bleed
100 ppm NO
7 ppm NO_2 in N_2 and Air
pH:4 Buffer Traps
pH:4 Buffer Traps
Sampling Pump
2 L/min
Sampling Pump
2 L/min

Figure: 3 Simulated Engine Run With PH: 4 Citrate Phosphate Buffer Traps

Table 2
Results of Artifact Experiments with Amine Added to pH 4 Citrate-Phosphate Buffer Traps During Engine Sampling

	Added Amine	Flow Rate (L/min)	Time (hr)	Results	Detection Light (μg/trap)
1.	50 μg/ morpholine	2.4	.5	No nitrosomorpholine formed	0.018
2.	50 μg pyrrolidine	2	1	No nitrosopyrrolidine formed	0.018
3.	50 μg dimethylamine	2.1	.5	0.1 $\mu g/m^3$ NDMA	0.006
	None	2.1	.5	0.1 $\mu g/m^3$ NDMA	0.006
4.	63 μg pyrrolidine	2.2	.5	No nitrosopyrrolidine formed	0.018
	63 μg pyrrolidine* $NO + NO_2$	2.2	.5	No nitrosopyrrolidine formed	0.018

*$NO + NO_2$ were bled into this sample (see text).

Table 3
Mack ETAY (B) 673A: Shell Rotella T SAE30
Nitrosamine and $NO.NO_2$ Measurements

Test Mode	NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/0.5hr$)	NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/0.5hr$)	$NO.NO_2 \times 10^{12}$	$\frac{NDMA(\mu g/0.5hr)}{NO.NO_2} \times 10^{-12}$
1	0.24							
1	0.24	0.24	0.5.	N.D.			68	0.007
2	0.49							
2	0.62	0.55	2.0	N.D.			5200	0.0004
3	0.37							
3	0.38	0.37	2.2	N.D.			8500	0.0002
4	0.42							
4	0.42	0.42	0.6	N.D.			68	0.009
5	0.66(0.57)*							
5	0.61	0.63	5.3.	N.D.			14000	0.0004
6	0.52							
6	1.30	0.91	4.4	N.D.			3400	0.001
7	0.51							
7	0.49(0.49)*	0.50	1.2	N.D.			200	0.006

N.D. - Not Detected
* - HPLC-TEA confirmation

Table 4
Mack ETAY (B) 673A: Amoco 300 SAE 30
Nitrosamine and NO.NO_2 Measurements

Test Mode	NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/m^3$)	Average NDMA (μg/0.5hr)	NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/m^3$)	Average NMOR (μg/0.5hr)	NO.NO_2 x 10^{12}	$\frac{\text{NDMA}(\mu g/0.5hr)}{\text{NO.NO}_2}$ x 10^{-12}
1	4.9(5.3)*	5.0	10.5	N.D.	N.D.	N.D.	100	0.1
1	5.1			N.D.				
2	3.6	4.2	15.1	N.D.	N.D.	N.D.	7100	0.002
2	4.9			N.D.				
3	3.8	3.8	22.8	0.4	0.35	2.1	12000	0.002
3	3.8			0.3				
4	2.0	1.8	2.7	N.D.	N.D.	N.D.	26	0.1
4	1.7			N.D.				
5	5.7(5.2)*	5.8	48.7	N.D.	N.D.	N.D.	11000	0.004
5	6.0			N.D.				
6	3.6	3.8	18.2	N.D.	N.D.	N.D.	5100	0.003
6	4.1			N.D.				
7	2.7	2.5	6.0	0.6	0.50	1.2	230	0.03
7	2.4			0.4.				

N.D. - Not Detected
* - HPLC-TEA confirmation

Table 5
Mack ETAY (B) 673A: Mobil Delvac 1200 SAE 30
Nitrosamine and NO.NO_2 Measurements

Test Mode	NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/0.5hr$)	NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/0.5hr$)	NO.NO_2x 10^{12}	$\frac{NDMA(\mu g/0.5hr)}{NO.NO_2} \times 10^{-12}$
1	20.6(18.4)*			0.9				
1	21.1	20.8	43.7	1.0	0.9	2.0	220	0.2
2	15.2			1.4				
2	15.3	15.2	54.7	N.D.	0.7	2.5	7400	0.007
3	12.2			1.7				
3	12.8	12.5	75.0	1.4	1.5	9.3	7400	0.01
4	9.5			0.8				
4	7.4	8.4	12.6	0.8	0.8	1.2	76	0.2
5	11.4			2.0				
5	11.6	11.5	96.6	2.3	2.1	18.1	12000	0.008
6	8.0			1.6				
6	6.9	7.4	35.5	0.8	1.2	5.8	4600	0.008
7	5.5			1.0				
7	6.8(6.7)*	6.1	14.6	0.9	0.9	2.3	180	0.08

N.D. - Not Detected
* - HPLC-TEA confirmation

Table 6
Mack ETAY (B) 673A: Mobil Delvac Super 15 W 40
Nitrosamine and $NO.NO_2$ Measurements

Test Mode	NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/0.5hr$)	NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/0.5hr$)	$NO.NO_2 \times 10^{12}$	$\frac{NDMA(\mu g/0.5hr)}{NO.NO_2} \times 10^{-12}$
1	30.7	28.0	58.8	0.9	0.8	1.8	77	0.8
1	25.3(26.8)*			0.8				
2	24.9	26.6	95.8	1.6	1.5	5.6	5400	0.02
2	28.3			1.5				
3	21.8	20.7	124.2	1.7	1.9	11.7	13000	0.009
3	19.7			2.2				
4	12.9	12.6	18.9	1.2	1.0	1.5	97	0.2
4	12.3			0.8				
5	16.9	16.0	134.4	1.8	1.8	15.5	15000	0.009
5	15.2			1.9				
6	10.6	10.8	51.8	1.4	1.6	7.9	4200	0.01
6	11.1			1.9				
7	7.6	7.7	18.5	0.8	0.8	2.0	270	0.07
7	7.9(6.0)*			0.9				

* - HPLC-TEA confirmation

Table 7
Detroit Diesel 6V71N; Mobil Delvac Super 15 W 40
Nitrosamine and $NO.NO_2$ Measurements

Test Mode	NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/0.5hr$)	NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/0.5hr$)	$NO.NO_2 \times 10^{12}$	$\frac{NDMA(\mu g/0.5hr)}{NO.NO_2} \times 10^{-12}$
1	2.5							
1	3.1	2.8	1.7	N.D.			3.1	0.5
2	3.9							
2	4.2	4.0	2.4	N.D.			1.7	1.4
3	5.2							
3	5.6	5.4	3.2	N.D.			11.4	0.3
4	3.8							
4	3.2	3.5	1.0	N.D.			3.6	0.3
5	6.0(6.0)*							
5	5.6	5.8	26.1	N.D.			19.3	1.3
6	3.2							
6	3.6	3.4	6.1	N.D.			4.9	1.2
7	1.4							
7	1.5(1.7)*	1.4	2.1	N.D.			1.2	1.7

N.D. - Not Detected
* - HPLC-TEA confirmation

Table 8
Caterpillar 3406; N; Mobil Delvac 15 W 40
Nitrosamine and $NO.NO_2$ Measurements

Test Mode	NDMA (μg/m)	Average NDMA (μg/m)	Average NDMA (μg/0.5hr)	NMOR (μg/m)	Average NMOR (μg/m)	Average NMOR (μg/0.5hr)	$NO.NO_2$x 10	NDMA(μg/0.5hr) / $NO.NO_2$
1	4.9(4.9)*			N.D.				
1	4.8	4.8	12.0	N.D.	N.D.	N.D.	2.7	4.4
2	5.3			0.4				
2	5.6	5.4	19.4	N.D.	0.2	0.7	51.4	0.4
3	5.8			N.D.				
3	6.1	5.9	34.2	0.9	0.4	2.6	88.6	0.4
4	1.6			N.D.				
4	1.8	1.7	4.6	N.D.	N.D.	N.D.	1.7	2.7
5	6.7(6.4)*			0.7				
5	6.1	6.4	35.6	0.8	0.7	4.0	510.6	0.07
6	4.9			0.4				
6	4.5	4.7	21.1	N.D.	0.2	0.9	116.8	0.2
7	1.8			N.D.				
7	2.0	1.9	6.8	N.D.	N.D.	N.D.	0*@	*@

N.D. - Not Detected
* - HPLC-TEA confirmation

*@ - Whereas there was 37 ppm NO_2, there was zero NO, leading to a zero product Of the two and an unquantifiable ratio of NDMA to $NO.NO_2$

Table 9
Mercedes-Benz: Mobil Delvac Super 15 W 40
Nitrosamine and $NO.NO_2$ Measurements

Vehicle Speed (mph)	NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/m^3$)	Average NDMA ($\mu g/0.5hr$)	NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/m^3$)	Average NMOR ($\mu g/0.5hr$)	$NO.NO_2 \times 10^{12}$	$NDMA \frac{(\mu g/0.5hr)}{NO.NO_2} \times 10^{-12}$
20	2.9	3.1	4.6	N.D.	N.D.	N.D.	2.5	1.2
20	3.3(3.7)*			N.D.				
50	4.6	4.6	9.2	0.3	0.1	0.3	4.8	0.9
50	4.6(5.0)*			N.D.				

N.D. - Not Detected
* - HPLC-TEA confirmation

Figure Captions:

Figure 4-a	GC-TEA Chromatogram of 4 ng NDMA Standard.
Figure 4-b	GC-TEA Chromatogram of a Crankcase Emission Sample Showing the presence of 25.3 $\mu g/m^3$ of NDMA.
Figure 4-c	HPLC-TEA Chromatogram of 10 ng NDMA Standard.
Figure 4-d	HPLC-TEA Chromatogram of a Crankcase Emission Sample Showing the presence of 26.8 $\mu g/m^3$ of NDMA.

The sample was collected from Mack ETAY(B) 673A engine operating with Mobil Delvac Super 15W40 oil in mode number 1.

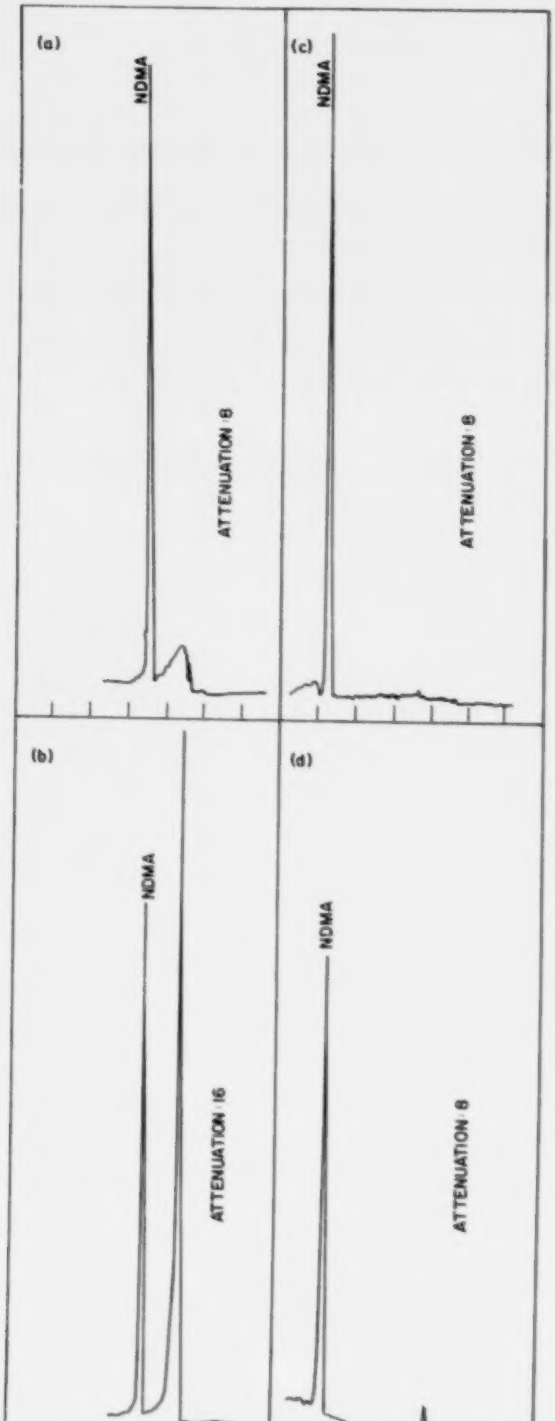

(a)
NDMA
ATTENUATION 8
(c)
NDMA
ATTENUATION 8
(b)
NDMA
ATTENUATION 16
(d)
NDMA
ATTENUATION 8
8 6 4 2 0
TIME (MINUTES)
8 6 4 2 0
TIME (MINUTES)

Figure: 4

Figure Captions:

Figure 5-a	GC-TEA Chromatogram of 4 ng NDMA Standard.
Figure 5-b	GC-TEA Chromatogram of a Crankcase Emission Sample Showing the presence of 6 $\mu g/m^3$ of NDMA.
Figure 5-c	HPLC-TEA Chromatogram of 16 ng NDMA Standard.
Figure 5-d	HPLC-TEA Chromatogram of a Crankcase Emission Sample Showing the presence of 6 $\mu g/m^3$ of NDMA.

The sample was collected from DDAD 6V-71N engine operating with Mobil Delvac Super 15W40 oil in mode 5.

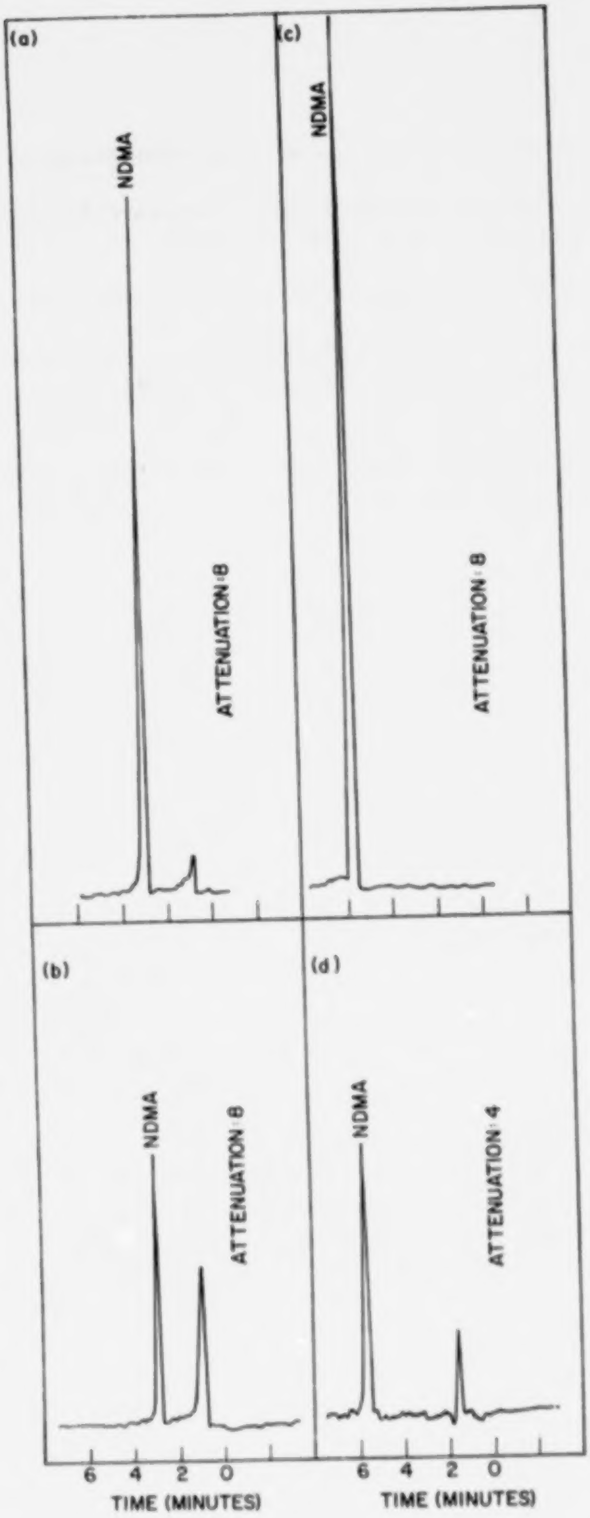

(a)
NDMA
ATTENUATION 8
(c)
NDMA
ATTENUATION 8
(b)
NDMA
ATTENUATION 8
(d)
NDMA
ATTENUATION 4
6 4 2 0
TIME (MINUTES)
6 4 2 0
TIME (MINUTES)

Figure: 5

Figure Captions:

Figure 6-a	GC-TEA Chromatogram of 4 ng NDMA Standard.
Figure 6-b	GC-TEA Chromatogram of a Crankcase Emission Sample Showing the presence of 6.7 $\mu g/m^3$ of NDMA.
Figure 6-c	HPLC-TEA Chromatogram of 10 ng NDMA Standard.
Figure 6-d	HPLC-TEA Chromatogram of a Crankcase Emission Sample Showing the presence of 6.4 $\mu g/m^3$ of NDMA.

The sample was collected from Caterpillar 3406 engine operating with Mobil Delvac Super 15W40 oil in mode 5.

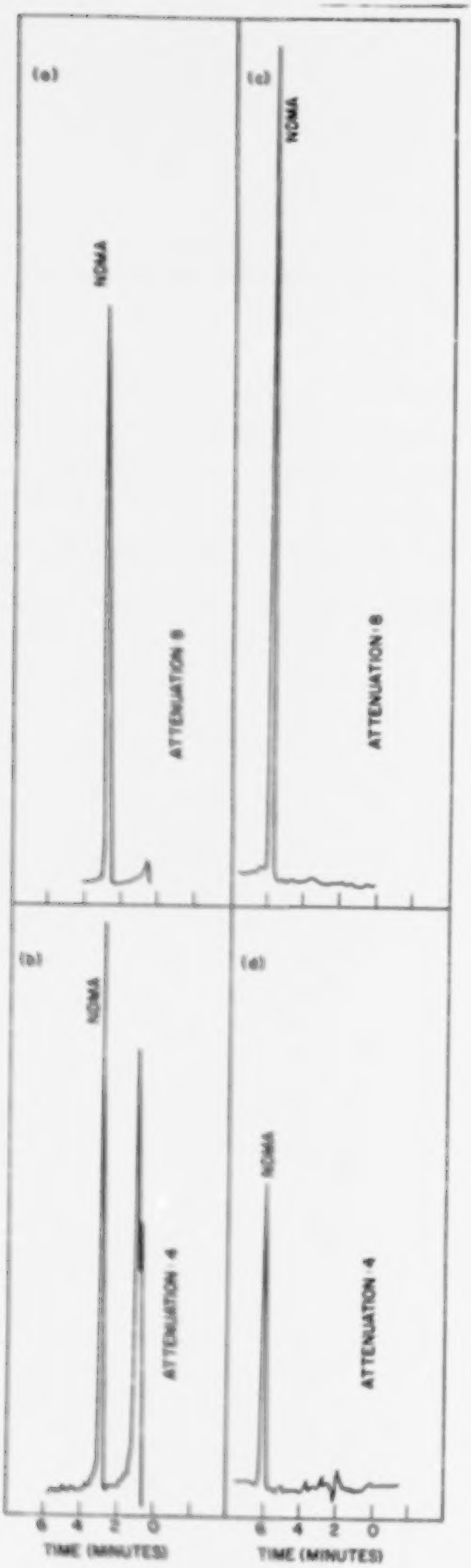

(a)
NDMA
ATTENUATION 8
(b)
NDMA
ATTENUATION 4
(c)
NDMA
ATTENUATION 8
(d)
NDMA
ATTENUATION 4
6 4 2 0
TIME (MINUTES)
6 4 2 0
TIME (MINUTES)

Figure: 6

Table 10
Confirmation of NMOR on GC-TEA and HPLC-TEA

Sample No.	Engine	Oil	GC-TEA (ppm)	HPLC-TEA (ppm)
1	Mack ETAY (B) 673A	Mobil Delvac Super 15 W 40	0.63	0.65
2	Mack ETAY (B) 673A	Mobil Delvac 1200	0.90	0.85
3	Mack ETAY (B) 673A	Amoco 300 SAE 30	0.10	0.10

Figure Captions:

Figure 7-a	GC-TEA Chromatogram of 2 ng NMOR Standard.
Figure 7-b	GC-TEA Chromatogram of Combined Crankcase Emission Samples showing the presence of 0.63 ppm of NMOR in solution.
Figure 7-c	HPLC-TEA Chromatogram of 5 ng NMOR Standard.
Figure 7-d	HPLC-TEA Confirmation of the combined Crankcase Emission Samples showing the presence of 0.65 ppm of NMOR in solution.

The samples were collected from Mack ETAY (B) 673A engine operating with Mobil Delvac Super 15W40 oil in modes 3 through 7 and then combined to increase the detection.

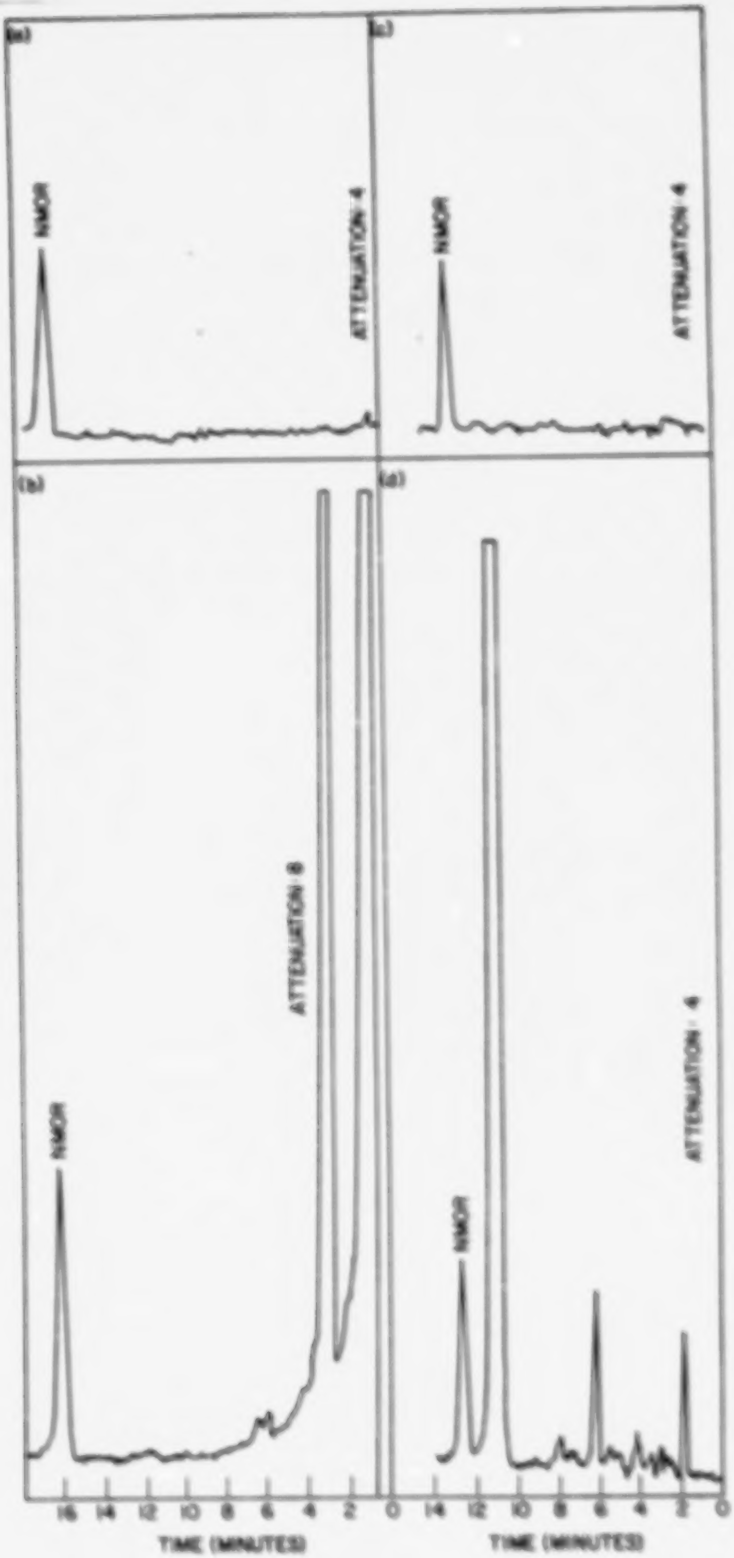

(a)
NMOR
ATTENUATION 4
(c)
NMOR
ATTENUATION 4
(b)
NMOR
ATTENUATION 8
(d)
NMOR
ATTENUATION 4
16 14 12 10 8 6 4 2 0
TIME (MINUTES)
14 12 10 8 6 4 2 0
TIME (MINUTES)

Figure: 7

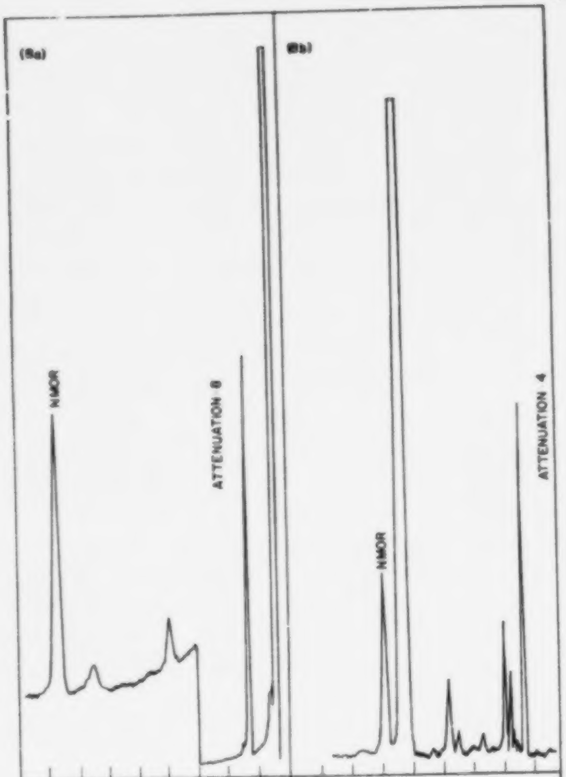
Figure Captions:

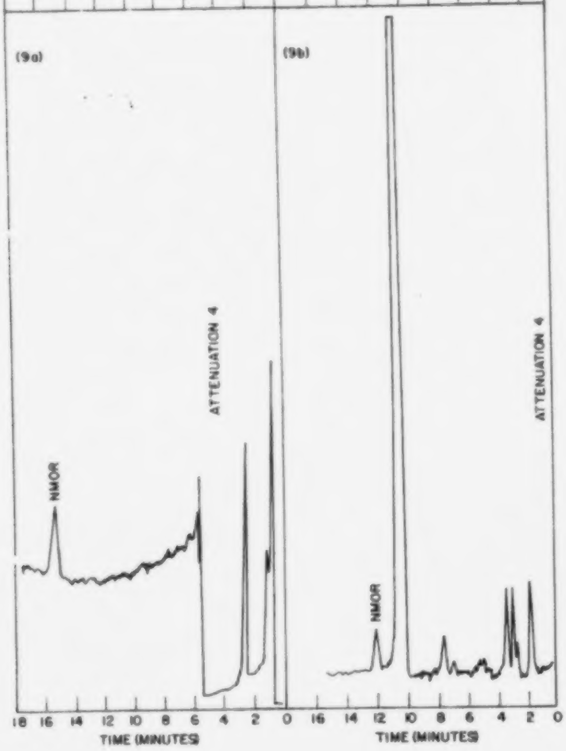
Figure 8-a	GC-TEA Chromatogram of combined Crankcase Emission Samples showing the presence of 0.90 ppm of NMOR in solution.
Figure 8-b	HPLC-TEA confirmation of the combined Crankcase Emission Samples showing the presence of 0.85 ppm of NMOR in solution.

The samples were collected from Mack ETAY (B) 673A engine operating with Mobil Delvac 1200 oil in modes 3 through 7 and then combined to increase the detection.

Figure 9-a	GC-TEA Chromatogram of combined Crankcase Emission Samples showing the presence of 0.10 ppm of NMOR in solution.
Figure 9-b	HPLC-TEA confirmation of the combined Crankcase Emission Samples showing the presence of 0.10 ppm of NMOR in solution.

The samples were collected from Mack ETAY (B) 673A engine operating with Amoco 300 SAE 30 oil in modes 3 through 7 and then combined to increase the detection.





Top Figure: 8
Bottom Figure: 9

were operated in parallel using different lengths of tubing between the crankcase and traps (1' vs. 6.5'). There was no increase in the levels of NDMA or NMOR with the longer sampling line. Checking for the formation of nitrosamines in the first few inches of sampling line was not deemed necessary since trucks normally release emissions through 2 to 3 feet of exhaust pipe.

The identity of NDMA from the liquid traps was established by observing the same quantitation at the appropriate chromatographic retention time on both GC and HPLC-TEA (see Tables 3-9 and Figures 4-6). Further confirmation was obtained by combining the liquid trap extracts from a single engine, concentrating to 1 ml, and examining the concentrate by GC-high resolution MS (see Appendix D for comparison of GC-TEA, GC-MS results).

The confirmation of NMOR on GC-MS could not be obtained due to the lack of sufficient amount of material. It's presence was confirmed on GC-TEA, HPLC-TEA on the combined samples from a single engine (see Table 10 and Figure 7, 8, 9).

2. Tests with ThermoSorb™/N Air Samplers and Sulfamic Acid Cartridges

As with the aqueous traps, recovery studies were conducted using a mixture containing 500 ng ech of NDMA, NDEA, NDPA, NDBA, NPiP, NPYR and NMOR. Three separate experiments were conducted; first with the ThermoSorb™/N Air Sampler alone, second with an empty cartridge folowed by a ThermoSorb™/N Air Sampler, third with a cartridge filled with sulfamic acid followed by a ThermoSorb™/N Air Sampler. The results, shown in Table 11, indicate that in spite of the pentane and DCM/pentane wash, 77 to 86% of the nitrosamines are recovered in the acetone fraction. By comparison, if acetone alone had been used, the recovery would have been 98-100% (Rounbehler, D.P. et al., 1980). The 'dead space' in an empty cartridge led to another 20 to 30% loss in recovery. Recovery with and without sulfamic acid in the cartridge was virtually identical.

ThermoSorb™/N Air Samplers have been tested for breakthrough, using the 7 test nitrosamines (Rounbehler, D.P. et al., 1980). Even after passing 2000 L of air at 2 L/min and 25°C through the cartridges, breakthrough was not observed.

Resistance to breakthrough was confirmed by using two ThermoSorb samplers in series during actual engine sampling. No detectable amounts of nitrosamines were found in the second cartridge. The stability of nitrosamines in the ThermoSorb samplers has been tested by the suppliers, and no significant losses were found even after 5 weeks of storage at room temperature (Rounbehler, D.P. and Reisch, J.W., 1979, unpublished results).

As with the liquid traps, the possibility that nitrosamines could be formed artifactually during collection and/or analysis, was tested both in the laboratory, and during tests on a diesel engine. For the laboratory simulation, a solution containing 1 part-per-thousand (by weight) of each amine, DMA, dipropylamine (DPA), Pip, PYR and MOR was introduced into the sulfamic acid cartridges at 6 min intervals (see Figure 10) for 1 hr. One cartridge received a total of 25 µg of each of the amines; the other cartridge received a total of 50 µg of each of the amines. The gas phase consisted of 100 ppm NO + 7ppm NO_2 in air; with the total NO_x passed over the cartridges during the run being 12 mg NO + 0.8 mg NO_2. Extraction of the ThermoSorb™/N Air Sampler, using techniques previously described and subsequent analysis, showed that in only one experiment was a trace of NMOR observed (see Table 12). The yield of NMOR observed (see Table 12). The yield of NMOR was approximately 0.03%, with the amount being observed virtually identical to the detection limit. For the other experiments, nitrosamines were not observed.

For the artifact tests on a diesel engine, only MOR was used, because it had been shown that MOR has the highest nitrosation rate with NO_x on solid

Table 11
Recoveries of Various Nitrosamines
(500 ng each) from Sulfamic Acid and ThermoSorb™/N Air Samplers

Nitrosamine	ThermoSorb™/N Air Sampler % Recovery	Empty Catridge and ThermoSorb™/N Air Sampler % Recovery	Sulfamic Acid and ThermoSorb™/N Air Sampler % Recovery
NDMA	77	57	61
NDEA	78	55	51
NDPA	79	56	44
NDBA	75	54	42
NPiP	81	58	53
NPYR	86	55	57
NMOR	83	53	58

* The recovery is the average of two measurements.

adsorbers (Goff, U.G. and Coombs, J.R., 1979, unpublished results) when compared with DMA, DPA, Pip and PYR. Fifty µg of MOR was introduced into the sulfamic acid cartridge at the beginning of the test. For one of the tests, additional nitrogen oxides such as 80 ppm NO and 6 ppm NO_2 (total added was 5.4 mg NO and 0.4 mg NO_2) were passed through the cartridges. The results, shown in Table 13, show that NMOR was not detected in any of the tests.

TASK II AND III. Engine Selection and Testing

The sample collection and preparation methods described in Section III. C, Task I were used to collect and analyze crankcase emission samples. The influence of the engine type was addressed by taking samples from three different heavy duty engines operated with the same type of oil and the influence of the oil type was considered by taking crankcase emission samples from the same heavy-duty engine after operation with four different oils. Also a LD diesel engine was sampled to see if it behaves similarly to HD diesel engines in producing nitrosamines. Mack ETAY (B) 673A engine crankcase emissions were sampled with Shell Rotella T SAE 30, Amoco 300 SAE 30, Mobil-Delvac 1200 SAE 30, Mobil Delvac Super 15-W-40 oils in separate runs. Other engines were samples with only Mobil Delvac Super 15-W-40 oil in the crankcase. Duplicate samples were taken and the results were averaged for each mode of the engine. The nitrosamine amounts were expressed as concentration ($\mu g/m^3$), and as mass flow ($\mu g/1/2$ hr) versus the product NO and NO_2 concentrations in the crankcase emissions. These results are presented in Tables 3 through 9.

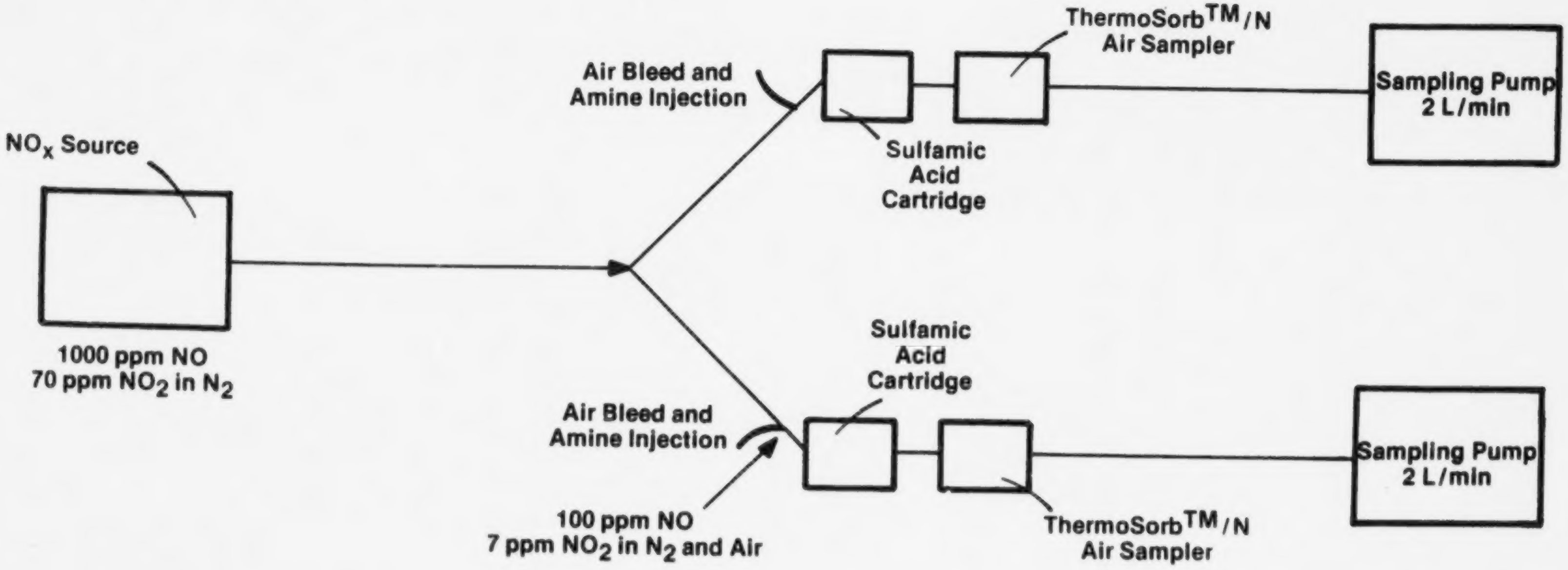

NO_x Source
1000 ppm NO
70 ppm NO_2 in N_2
Air Bleed and
Amine Injection
Sulfamic
Acid
Cartridge
ThermoSorb^{TM}/N
Air Sampler
Sampling Pump
2 L/min
Air Bleed and
Amine Injection
100 ppm NO
7 ppm NO_2 in N_2 and Air
Sulfamic
Acid
Cartridge
ThermoSorb^{TM}/N
Air Sampler
Sampling Pump
2 L/min

Figure : 10 Simulated Engine Run with Sulfamic Acid, ThermoSorb^{TM}/N Air Sampler

Table 12

Results of Artifact Experiments with Sulfamic Acid and ThermoSorb™/N Air Sampler Under Simulated Engine Conditions

Added Amine	Nitrosamine Detected	Detection Limit (μg/cartridge)
25 & 50 μg Dimethylamine	None	0.006
25 & 50 μg Dimpropylamine	None	0.012
25 & 50 μg Piperidine	None	0.016
25 & 50 μg Pyrrolidine	None	0.016
25 μg Morpholine	None	0.016
50 μg Morpholine	0.016 μg NMOR*	0.016

*The amount observed was at the detection limit.

Table 13
Results of Artifact Experiments with Sulfamic Acid and ThermoSorb™/N Air Sampler Under Actual Engine Conditions

Experiment	Added Amine*	Flow Rate (L/min)	Time (hr)	Nitrosamine Detected	Detection Limit (μg/sampler)
A	50 μg morpholine	2.3	0.5	None	0.018
B	50 μg morpholine	2.2	0.5	None	0.018
C**	50 μg morpholine	2.2	0.5	None	0.018

* The amine was added to the sulfamic acid trap; nitrosamines were looked for in the following ThermoSorb™/N Air Sampler trap.

** This sample received extra NO + NO_2 (see text).

TASK IV. Oil Analysis Method Development for Nitrosamine

These analyses were carried out by bubbling air at 0.5 L/min. for one hour through a 50 g oil sample which was maintained at 110°C. Ascorbic acid (0.5 g in 1 ml water) and DL-α-tocopherol were added to the oil to inhibit in situ nitrosation (Mergens, W.J. et al., 1978; Archer, M.C. et al., 1975; Fiddler, W. et al., 1973). The apparatus used is shown in Figure 11. Nitrosamines were collected on a ThermoSorb™/N Air Sampler, and eluted as described earlier (see Figure 2). An aliquot of the acetone fraction was introduced into the GC-TEA and/or HPLC-TEA for analysis.

Artifact Control Experiments

A recovery study was conducted by adding a mixture of nitrosamines at 1 part-per-billion (ppb) and 10 ppb levels to a nitrosamine-free oil sample. The recovery data and detection limits of nitrosamines in the oil are shown in Table 14. A GC-TEA chromatogram of the spiked sample, Figure 12, is also attached. The recoveries from oil samples spiked at 1 ppb level were lower than the recoveries at 10 ppb level. The lower recoveries might be attributed to systematic errors. The possibility of artifactual formation of nitrosamines during the analysis was also checked. Five amines, DMA, DPA, PiP, PYR, and MOR (50 μg each), were added to a nitrosamine-free oil and the oil was analyzed as in the test samples. In no case was the nitrosamine derivative found to be present. In a second test, 50 μg of each amine was added to the ThermoSorb™/N Air Sampler and the experiment repeated. Again, no trace of the nitrosamine derivative could be detected. The absence of any nitrosamine peak in these experiments also proves that the air and ThermoSorb™/N Air Sampler used contained no preformed nitrosamines. The air used was checked for the presence of nitrosating agents by placing a morpholine spiked (50 μg) ThermoSorb™/N Air

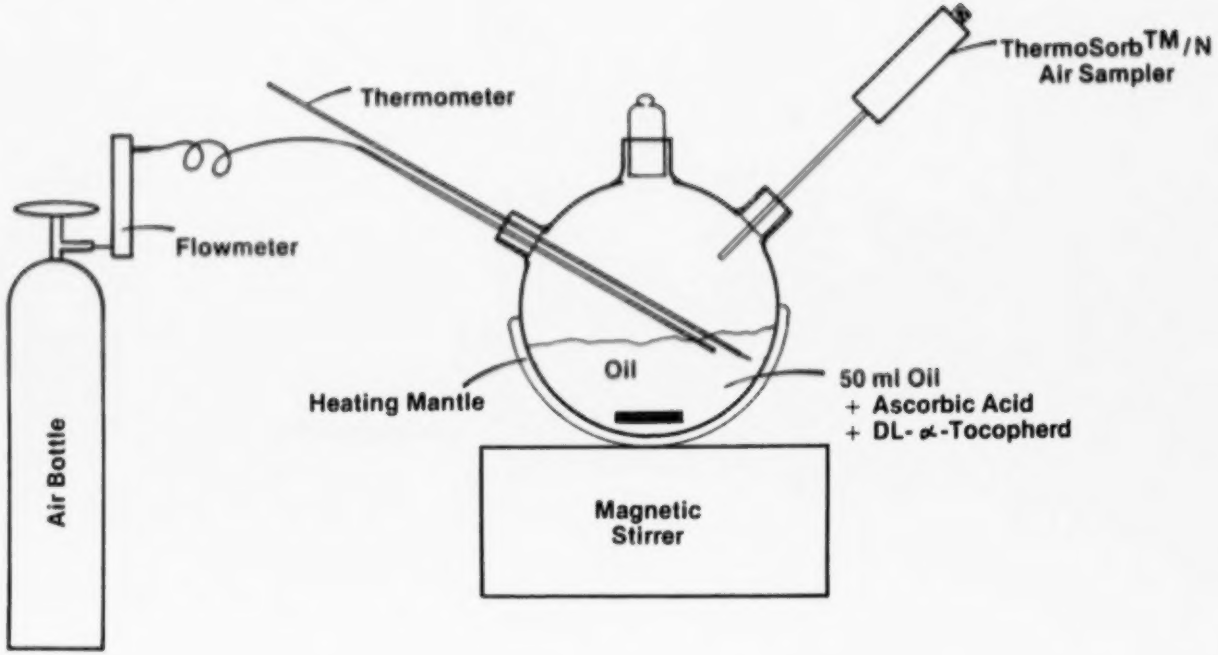

ThermoSorb™/N
Air Sampler
Thermometer
Flowmeter
Oil
Heating Mantle
50 ml Oil
+ Ascorbic Acid
+ DL-α-Tocopherd
Magnetic
Stirrer
Air Bottle

Figure: 11 Oil Nitrosamine Collection Apparatus

Table 14

Recovery of Various Nitrosamines From Oil Samples

Nitrosamine	Recovery (%)* 10 ppb	Recovery (%)* 1 ppb	Detection Limit in Oil (ppb)
Nitrosodimethylamine	73	48	0.1
Nitrosodiethylamine	77	40	0.2
Nitrosodipropylamine	56	34	0.3
Nitrosodibutylamine	25	28	1.0
Nitrosopiperidine	47	22	0.7
Nitrosopyrrolidine	55	34	0.4
Nitrosomorpholine	66	42	0.5

*Average of two measurements

Figure Captions:

Figure 12-a	GC-TEA Chromatogram of 2 ng mixture of NDMA, NDEA, NDPA, NDBA, NPiP, NPYR, and NMOR.
Figure 12-b	GC-TEA Chromatogram of an Oil Sample to Which a Standard Mixture of 7 nitrosamines (NDMA, NDEA, NDPA, NDBA, NPiP, NPYR, NMOR) had been added, each at the 1 ppb level.

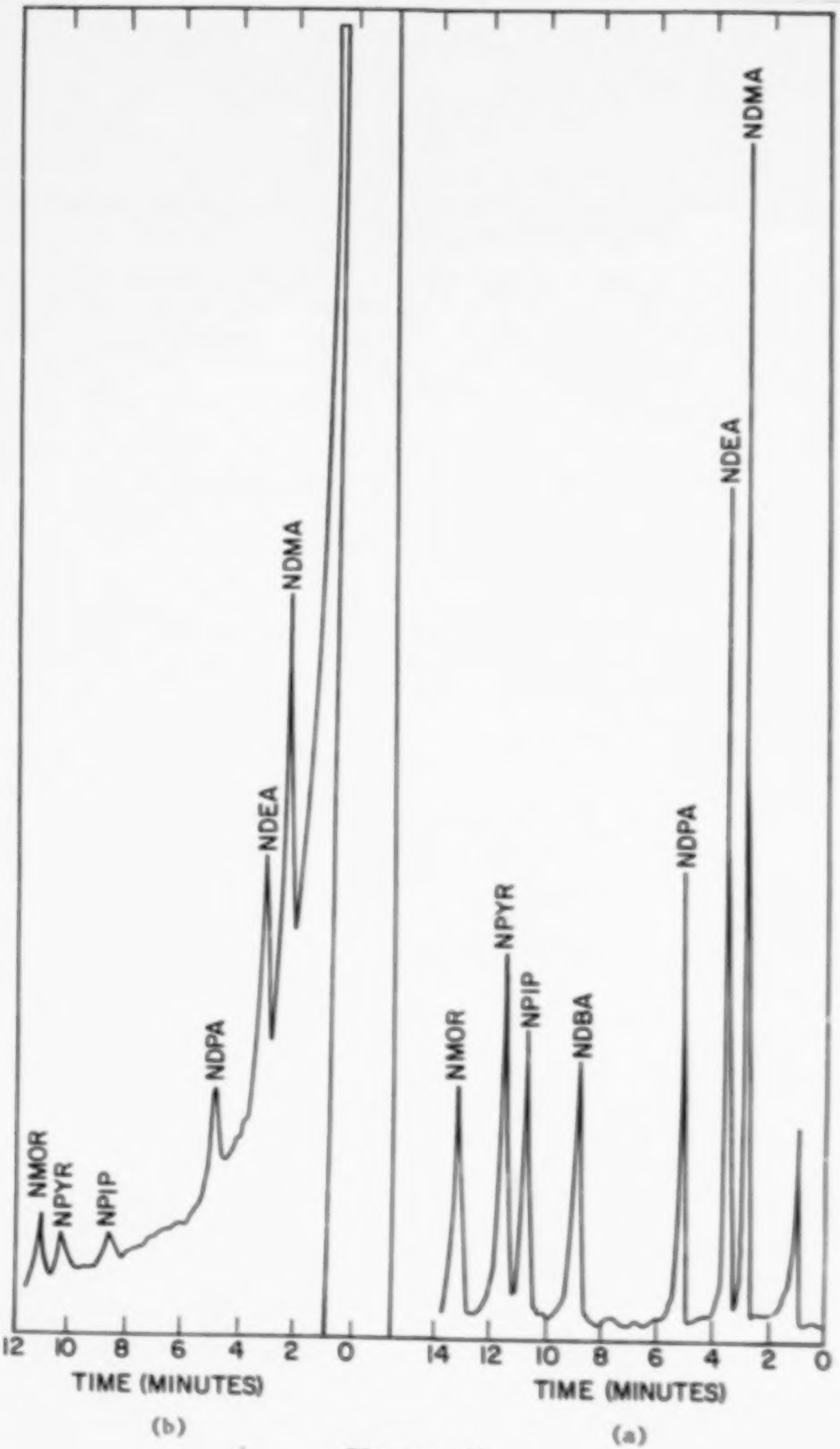

NMOR
NPYR
NPIP
NDPA
NDEA
NDMA
12
10
8
6
4
2
0
TIME (MINUTES)
(b)
NMOR
NPYR
NPIP
NDBA
NDPA
NDEA
NDMA
14
12
10
8
6
4
2
0
TIME (MINUTES)
(a)

Figure: 12

Sampler at the air inlet of the flask. There was no formation of NMOR (detection limit: 0.016 μg per sampler).

A stability study of nitrosamines in oils was conducted by analyzing different portions of the same oil which were exposed to different conditions. The results are given in Table 15. Although the results for Mobil Delvac 1200 obtained at 42nd hr of usage are not significantly different, the data from 65th hr sample might suggest that some nitrosamine deterioration is occuring under storage conditions, but not enough samples were available for analysis to permit any statistically significant results.

TASK V. Selection and Survey of the Oil Samples

A nitrosamine survey of unused and used oils was conducted. Unused oils were surveyed to determine the effect of the oil type and different additives. These oils were supplied by oil companies and SWRI or purchased by the New England Institute for Life Sciences. The oils supplied by SWRI were taken from various barrels and quart cases from their in-house stock and shipped to us by Federal Express. The samples obtained by the New England Institute for Life Sciences were purchased in quart size cans. Oil samples obtained from oil companies were requested by the EPA project officer and shipped to us in pint and quart size cans.

Used oil samples were surveyed to determine the effect of the usage duration on the nitrosamine levels. These samples were supplied by the engine manufacturers upon request by the EPA project officer. They were collected after various intervals of usage and shipped in pint size cans or plastic containers via UPS, Emery Air Freight or Federal Express and were refrigerated upon arrival at our laboratories. The information supplied by the various engine manufacturing and oil companies is given in Appendix E.

Some used oil samples were acquired by the New England Institute for Life Sciences from auto service and repair stations and gas stations around the Boston area. 100 ml plastic bottles were left with the cooperating station and then picked up in 1-6 days. They were refrigerated upon receipt.

Except for the Amoco 300 SAE 30, the oils that were used in SWRI engines for crankcase emissions testing were acquired in Texas by SWRI. The Amoco oil was supplied by Amoco Oil Company from their Whiting refinery in Chicago.

We initially obtained some oil from Amoco Houston refinery to be used in SWRI test engines. Nitrosation of this oil produced (Table 16, Sample NO. 46) much less amounts of NDMA as compared to the one obtained from Amoco Whiting refinery (Table 16, Sample No. 11). For that reason, Amoco 300 SAE 30 (Table 16, Sample No. 59) was obtained from Whiting refinery at the time of SWRI engine testing. The difference between the two can be explained by the different additive package used in these oils.

Oil analysis methods described in Section III, Task IV were used for determining the volatile nitrosamine levels in the used and unused oils. The results are given in Table 16. The results of the used oil samples acquired by the New England Institute for Life Sciences are given in Appendix F. Later results must be regarded cautiously since the origin and handling of the samples could not be supervised.

TASK VI. Oil Nitrosation Method

This method was developed so as to simulate the nitrosation conditions which may be occuring in a typical engine. Using nitrogen oxides as the nitrosating agent, amines present in the oil would be nitrosated to give their corresponding nitrosamines. Fifty gram samples of used or unused oils were heated for one hour at 110°C while a gas mixture containing 100 parts-per-billion (ppm) NO + 7 ppm NO_2 in nitrogen was bubbled through at a rate of 2 L/min (12 mg NO + 0.8 mg NO_2 total introduced into the samples). Nitrosation inhibitors were not added to the oil. Nitrosamines were collected on

(cont. on pg. IV-1)

Table 15
Stability of NDMA in Oil Under Different Conditions

Oil	Condition	NDMA (ppb) GC-TEA
Mobil Delvac 1200, 42*	analyzed upon receipt	1.5
" "	refrigerated for 2 days	1.4
" "	kept at room temperature (R.T.) for 2 days	1.6
" "	heated at 50-55°C for 75 min.	1.8
" "	0.5 gm ascorbic acid + 100 mg DL α-tocopherol and kept at R.T. for 2 days	1.6
Mobil Delvac 1200, 65**	analyzed upon receipt	2.0
" "	refrigerated for 10 days	1.9
" "	kept at R.T. for 10 days	1.5

* This oil was analyzed after being in test engine (Mack 676 ENDT) for 42 hours.

**This oil was analyzed after being in test engine (Mack 676 ENDT) for 65 hours.

Table 16
Oil Analysis and Nitrosation Results

Sample No.	Oil	As Received NDMA (ppb) GC-TEA	As Received NMOR (ppb) GC-TEA	Nitrosated NDMA (ppb) GC-TEA	Nitrosated NMOR (ppb) GC-TEA
	Oils Supplied by SWRI				
2	Mobil Delvac 1230 SAE 30	N.D.	N.D	22.0(22.0)(a)	4.0(4.3)(a)
3	Texaco Ursa Super 3 SAE 30	N.D.	N.D.	8.0	1.5
7	Gulf Lube X.H.D. SAE 30	N.D.	N.D.	3.6	2.1
8	Chevron Delo 300 SAE 30	N.D.	N.D.	0.8	N.D.
11	Amoco 300 SAE 30	N.D.	N.D.	54.0(54.0)(a)	2.4(a)
13	Shell Rotella 30	N.D.	N.D.	2.4	5.6
14	Shell Rotella T. 15-W-40	N.D.	N.D.	1.0	1.4
46	Amoco 300 SAE 30 (b)	N.D.	N.D.	11.8	N.D.
	Oils Obtained by New England Institute for Life Sciences Around Boston Area				
9	Mobil Delvac 1200 SAE 30	N.D.	N.D.	18.0	N.D.
10	Volvoline SAE 30	N.D.	N.D.	2.0	0.8
12	Mobil Heavy Duty SAE 30	N.D.	N.D.	36.0(29.0)(a)	2.4
20	Chevron Delo 400 SAE 30	N.D.	N.D.	1.6	N.D.
	Gasoline Engine Oils Obtained by New England Institute for Life Sciences Around Boston Area				
47	Texaco Havolin SAE 30	N.D.	N.D.	24.0	1.2
48	Citgo Multigrade SAE 30	N.D.	N.D.	N.D.	N.D.
49	Gulfpride Multi 6 10W-20W-40	N.D.	N.D.	21.0	2.4
50	Quaker State 10-W-40	N.D.	N.D.	2.7	1.2
51	Pennzoil Multi-Vis SAE 10-W-30	N.D.	N.D.	N.D.	N.D.
52	Mobil Special 10-W-30	N.D.	N.D.	17.4	3.3
53	Exxon Uniflo 10-W-40	N.D.	N.D.	1.1	N.D.
54	Shell Fire and Ice 10-W-40	N.D.	N.D.	18.5	13.7
55	Mobil Super 10-W-40	N.D.	N.D.	38.0	2.4

Footnotes to Table 16:
(a) Confirmed on HPLC-TEA.
(b) Amoco oil from Houston Refinery.
(c) Amoco oil from Whiting Refinery in Chicago.
(d) Base oil stock. Since nitrosation of this base oil stock did not produce any nitrosamines, it suggests that the nitrosamines produced in oils are being produced as a result of the oil additives.

N.D. Not detected
--- Not analyzed

Table 16 (cont.)
Oil Analysis and Nitrosation Results

Sample No.	Oil	As Received NDMA (ppb) GC-TEA	As Received NMOR (ppb) GC-TEA	Nitrosated NDMA (ppb) GC-TEA	Nitrosated NMOR (ppb) GC-TEA
	Oils Obtained by New England Institute for Life Sciences in Arizona				
4	Shell Rotella T Premium Multi-Purpose SAE 30	N.D.	N.D.	1.8	N.D.
	Oils Supplied by Amoco(c)				
15	Amoco 300 SAE 15-W-40	0.35	N.D.	6.2	N.D.
75	Amoco HX 40(d)	N.D.	N.D.	N.D.	N.D.
1	Amoco 300 SAE 30	N.D.	N.D.	64.0(59)(a)	2.8(2.7)(a)
6	Amoco 200 SAE 30	N.D.	N.D.	3.1	N.D.
	Oils Supplied by Arco				
5	Arco Fleet S-3 plus SAE 30	N.D.	N.D.	4.8	N.D.
16	Arco Fleet S-3 plus 15-W-40	N.D.	N.D.	2.0	3.3
	Oils Supplied by Volvoline Oil Company				
17	Volvoline 15W-20W-40 All Fleet	N.D.	N.D.	0.8	N.D.
18	Volvoline SAE 30 All Fleet	N.D.	N.D.	1.6	N.D.
19	Volvoline HD Super HPD SAE 30, Detergent	N.D.	N.D.	N.D.	N.D.
	Oils Supplied by Mobil Oil Corporation				
21	Mobil Delvac 1230	N.D.	N.D.	15.0	7.7
22	Mobil Delvac Super 15-W-40	N.D.	N.D.	39.0(42.0)(a)	1.0
43	Mobil Delvac 1	0.45	N.D.	2.4	N.D.

Table 16 (cont.)
Oil Analysis and Nitrosation Results

		As Received		Nitrosated	
Sample No.	Oil	NDMA (ppb) GC-TEA	NMOR (ppb) GC-TEA	NDMA (ppb) GC-TEA	NMOR (ppb) GC-TEA
	Oils Supplied by Exxon				
23	Exxon HDX Plus 30	N.D.	N.D.	1.0	N.D.
24	Exxon XD-3-30	N.D.	N.D.	1.4	N.D.
25	Exxon 2118-S-3; 15-W-40	N.D.	N.D.	0.8	N.D.
	Oils Supplied by Gulf Oil Company				
26	Gulf Super Duty 30 LS-8645	N.D.	N.D.	1.3	N.D.
27	Gulf Lube X.H.D. 10-W-30 LS-8648	N.D.	N.D.	0.8	N.D.
28	Gulf Super Duty 15-W-40 LS-8646	N.D.	N.D.	1.3	N.D.
29	Gulf Lube X.H.D. 30 LS-8647	N.D.	N.D.	0.7	N.D.
	Oils Supplied by Chevron				
30	Chevron Delo 100 SAE 30	N.D.	N.D.	0.5	N.D.
31	Chevron Delo 200 SAE 30	N.D.	N.D.	1.2	N.D.
34	Chevron Delo 300 SAE 30	N.D.	N.D.	1.0	N.D.
32	Chevron Delo 400 SAE 30	N.D.	N.D.	N.D.	N.D.
33	Chevron Delo 400 15-W-40	N.D.	N.D.	5.4	N.D.
	Oils Supplied by Texaco				
37	Texaco Ursa Super 3 SAE 30	3.7	N.D.	4.8	N.D.
38	Texaco Ursa Extra Duty SAE 30	N.D.	N.D.	1.1	N.D.
39	Texaco Ursa Super Plus SAE 30	N.D.	N.D.	1.2	0.5
40	Texaco Ursa Plus 15-W-40	N.D.	N.D.	N.D.	2.4

Table 16 (cont.)
Oil Analysis and Nitrosation Results

Sample No.	Oil	As Received NDMA (ppb) GC-TEA	As Received NMOR (ppb) GC-TEA	Nitrosated NDMA (ppb) GC-TEA	Nitrosated NMOR (ppb) GC-TEA
	Oils Used in SWRI Engines				
44	Fresh Shell Rotella T SAE 30	N.D.	N.D.	0.8(0.8)(a)	N.D.
60	Used Shell Rotella T SAE 30 (8.6-hr sample; Mack)	N.D.	N.D.	0.6(0.8)(a)	N.D.
59	Fresh Amoco 300 SAE 30 (c)	N.D.	N.D.	25.0(24.0)(a)	N.D.
61	Used Amoco 300 SAE 30 (6.6-hr sample; Mack)	0.2	N.D.	3.0(a)	N.D.
45	Fresh Mobil Delvac 1200 SAE 30	N.D.	N.D.	88.2(82.0)(a)	25.4
62	Used Mobil Delvac 1200 SAE 30 (6.0-hr sample; Mack)	0.4	N.D.	5.7	1.5
58	Fresh Mobil Delvac Super 15-W-40	N.D.	N.D.	202.0(191.0)(a)	23.5
63	Used Mobil Delvac Super 15-W-40 (7.2-hr sample; Mack)	0.8	N.D.	15.0	3.3
64	Used Mobil Delvac Super 15-W-40 (5.5-hr sample; DDAD)	0.1	N.D.	42.2	11.2
65	Used Mobil Delvac Super 15-W-40 (5.6-hr sample; Cat)	0.4	N.D.	12.7	5.4
66	Used Mobil Delvac Super 15-W-40 (3.0-hr sample; Mercedes)	0.8	N.D.	48.4	8.8
	Oils Supplied by Deutz Diesel Limited				
35	Fresh Shell Rotella S 30	N.D.	N.D.	2.6	156.0
41	Used Shell Rotella S 30 (75.5-hr; sample)	0.8	N.D.	1.4	2.0
42	Used Shell Rotella S 30 (154.2-hr; sample)	N.D.	N.D.	N.D.	0.3
36	Used Shell Rotella S 30 (166.0.hr; sample)	N.D.	N.D.	N.D.	0.4

Table 16 (cont.)
Oil Analysis and Nitrosation Results

Sample No.	Oil	As Received NDMA (ppb) GC-TEA	As Received NMOR (ppb) GC-TEA	Nitrosated NDMA (ppb) GC-TEA	Nitrosated NMOR (ppb) GC-TEA
	Oils Supplied by Detroit Diesel Allison				
71	Fresh Texaco Ursa ED 30	N.D.	N.D.	N.D.	N.D.
73	Used Texaco Ursa ED 30 (75-hr; sample)	N.D.	N.D.	-	-
72	Used Texaco Ursa ED 30 (150-hr; sample)	N.D.	N.D.	-	-
74	Used Texaco Ursa ED 30 (217-hr; sample)	N.D.	N.D.	N.D.	N.D.
	Oils Supplied by Caterpillar Tractor Company				
79	Fresh Chevron RPM Delo 300 (30W)	N.D.	N.D.	0.6	N.D.
80	Used Chevron RPM Delo 300 (30W) (75-hr; sample)	N.D.	N.D.	-	-
81	Used Chevron RPM Delo 300 (30W) (150-hr; sample)	N.D.	N.D.	-	-
82	Used Chevron RPM Delo 300 (30W) (250-hr; sample)	N.D.	N.D.	N.D.	N.D.
83	Fresh Amoco 300 15-W-40	N.D.	N.D.	1.7	N.D.
84	Used Amoco 300 15-W-40 (50-hr; sample)	N.D.	N.D.	-	-
85	Used Amoco 300 15-W-40 (75-hr; sample)	0.2	N.D.	-	-
86	Used Amoco 300 15-W-40 (150-hr; sample)	N.D.	N.D.	N.D.	N.D.
87	Fresh Chevron RPM Delo 400 (30W)	N.D.	N.D.	N.D.	N.D.
89	Used Chevron RPM Delo 400 (30W) (150-hr; sample)	N.D.	N.D.	-	-
90	Used Chevron RPM Delo 400 (30W) (250-hr; sample)	0.4	N.D.	N.D.	N.D.

Table 16 (cont.)
Oil Analysis and Nitrosation Results

Sample No.	Oil	As Received NDMA (ppb) GC-TEA	As Received NMOR (ppb) GC-TEA	Nitrosated NDMA (ppb) GC-TEA	Nitrosated NMOR (ppb) GC-TEA
	Oils Supplied by Mack Truck, Inc.				
76	Fresh Mobil Infilrex 205	N.D.	N.D.	161.0	13.3
77	Used Mobil Infilrex 205 (75-hr; sample Unit 212)	0.2	N.D.	1.1	N.D.
78	Used Mobil Infilrex 205 (75-hr; sample Unit 211)	0.3	N.D.	N.D.	N.D.
91	Used Mobil Infilrex 205 (150-hr; sample Unit 211)	N.D.	N.D.	-	-
92	Used Mobil Infilrex 205 (300-hr sample; Unit 212)	N.D.	N.D.	N.D.	N.D.
	Oils Supplied by Cummins Engine Company, Inc.				
67	Fresh Shell Rotella T	N.D.	N.D.	N.D.	N.D.
68	Used Shell Rotella T (5749 mi on oil)	N.D.	N.D.	N.D.	N.D.
69	Used Shell Rotella T (11,427 mi on oil)	N.D.	N.D.	N.D.	N.D.
70	Used Shell Rotella T (15,000 mi on oil)	N.D.	N.D.	53.3	1.2
93	Fresh Chevron Delo 100 30W	N.D.	N.D.	N.D.	5.4
94	Used Chevron Delo 100 30W (6000 mi on oil)	N.D.	-	N.D.	N.D.
95	Used Chevron Delo 100 30W (11000 mi on oil)	N.D.	N.D.	N.D.	N.D.
96	Used Chevron Delo 100 30W (15000 mi on oil)	N.D.	-	0.9	N.D.

ThermoSorb™/N Air Sampler attached to the gas outlet of the oil containing flask and eluted using the procedures described above (see Figure 2).

TASK VII. Survey of the Nitrosability of the Oils

Using the method in section III, Task VI, unused and used oil samples were nitrosated. The results are given in Table 16. This technique was used to correlate the nitrosation potential of the oil with the actual nitrosamine emissions from the diesel engine crankcase (see Table 17, Figure 13).

IV. DISCUSSION OF RESULTS

It has been conclusively shown that the analytical methods developed here for the analysis of crankcase emissions were not prone to artifacts. It has been demonstrated that even the presence of nitrosamine precursors in the traps in relatively large amounts did not produce nitrosamines, both under normal engine test conditions, and also under artificially elevated NO_x levels.

The absence of any nitrosamines in simulation experiments also proved that the traps didn't contain any preformed nitrosamines or their precursors that might nitrosate under engine sampling conditions.

NDMA levels were the same (within experimental error) in pH 4 phosphate citrate buffer traps and in sulfamic acid/ThermoSorb™/N Air Samplers when sampling was done using these traps in parallel on actual crankcase samples (See Tables 3-9 for the results of parallel sampling with pH 4 phosphate citrate buffer traps and sulfamic acid/ThermoSorb™/N Air Samplers.) Such duplication of the NDMA levels in completely different trapping systems is further indication that the two techniques are artifact free.

The detection limit for both trapping methods was about 100 μg/m^3 for 60L of crankcase emission samples. The nitrosamines that were extracted from the traps were analyzed on GC-TEA and HPLC-TEA. Analysis on both systems serves as a good confirmatory technique. In GC, nitrosamines elute as a function of their

Table 17

Oil	NDMA in Nitrosated Oil (ppb)	Average NDMA* in emission (μg/0.5 hr)
1	1	2
2	25	18
3	88	48
4	200	72

Oil 1 Shell Rotella T SAE 30
2 Amoco 300 SAE 30
3 Mobil Delvac 1200 SAE 30
4 Mobil Delvac Super 15 W 40

* NDMA levels were measured in Mack ETAY (B) 673A engine.

** r (correlation coefficient), was obtained from the least-squares linear regression analysis of the two variables, namely NDMA in nitrosated oils and averaged NDMA in emissions.

Figure Captions:

Figure 13	Correlation between the NDMA levels in the nitrosated oils and in the crankcase emissions from Mack ETAY (B) 673A engine.

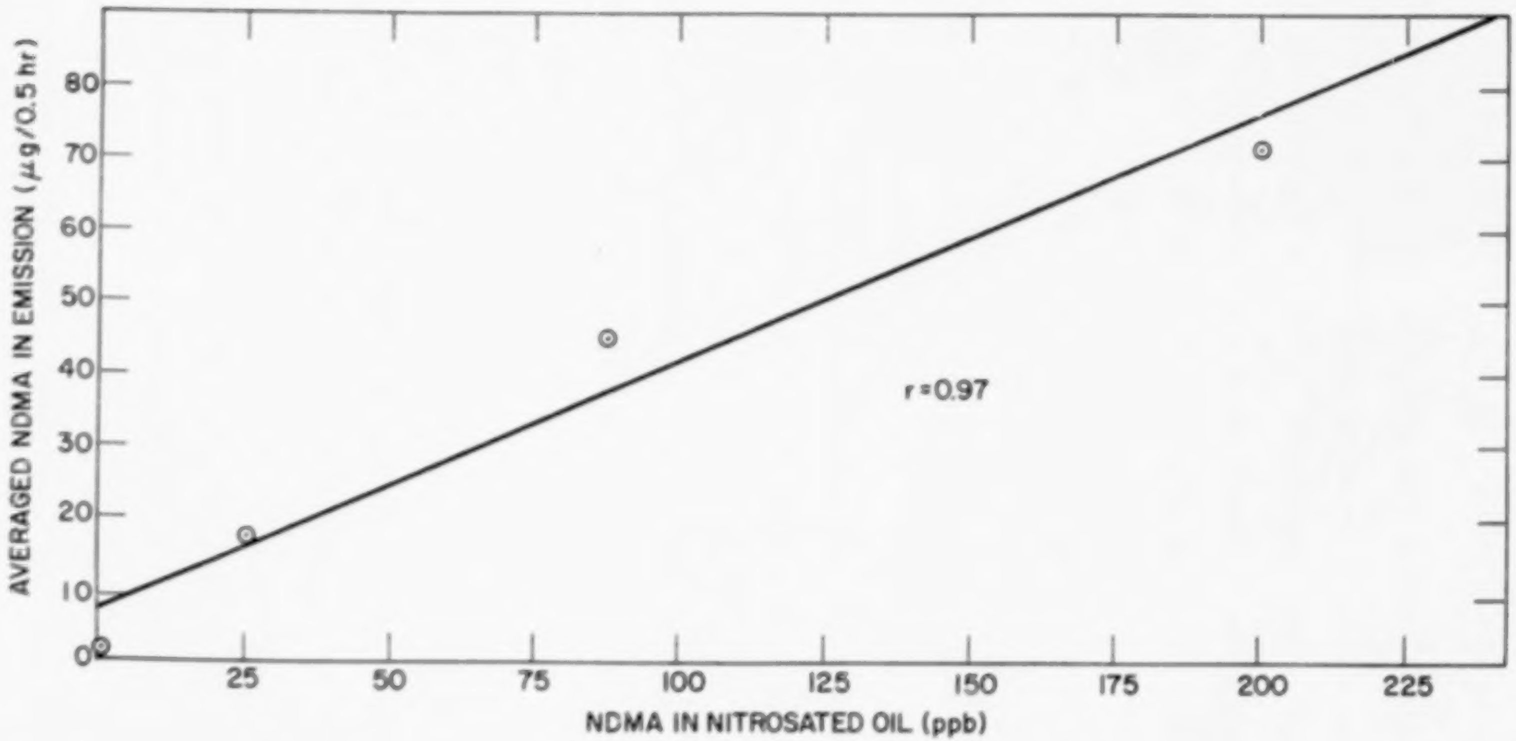

AVERAGED NDMA IN EMISSION (μg/0.5 hr)
0
10
20
30
40
50
60
70
80
r=0.97
25
50
75
100
125
150
175
200
225
NDMA IN NITROSATED OIL (ppb)

Figure: 13

relative vapor pressures, and solubility in the liquid phase. In HPLC, the nitrosamines generally elute according to their polarity, solubility in the liquid phase, and/or ionic properties. Because of the difference in these physical properties, the elution order of a series of compounds by GC and HPLC is different. If a selective detector such as the TEA is used for both GC and HPLC, the possibility of a coeluting peak giving a response in both systems is extremely small. Identification is considered positive if two criteria are met: 1) a single peak eluting at the known GC retention time of a standard is observed and 2) the magnitude of the GC-TEA and HPLC-TEA peaks are identical. See Tables 3 through 9 and Figures 4 through 9 for the GC-TEA and HPLC-TEA confirmation of NDMA and NMOR peaks. Further confirmatory evidence as to the identity of the nitrosamines was obtained by GC-high resolution MS (See Appendix D).

Nitrosamine levels in the crankcase emissions will be discussed according to the effects of three variables: nitrogen oxide levels in the crankcase emissions, amine levels in the oils and the effects of crankcase flow rates. Other influential engine variables can't be pinpointed at this time but there is some evidence that they exist. Obviously amines in the oils and the nitrogen oxides in the emissions are the main parameters, and, depending on the type of oil and type of engine used, one or the other can be the limiting factor in determining the nitrosamine levels.

Nitrosation of oil samples before and after use in the SWRI test engines indicated that used oils did not as readily produce nitrosamines as the corresponding unused oils (see Table 16, Oils Used in SWRI Engines). This result suggests that the nitrosamine precursors in the oil are somehow used up or otherwise removed from the process. Since production of nitrosamines from nitrosated oils suggests that the nitrosamine precursors in the oil are the main source of nitrosamines found in crankcase emissions, then one would expect a decrease in crankcase emission nitrosamine concentrations as the time the oil has been in the crankcase increases and, correspondingly, the nitrosability of the oil decreases (see Table 16).

According to the data obtained from the engine crankcase emissions however, this reduction of nitrosamine concentration in the emissions as a function of the operating times of the experiments did not occur (see Tables 3 through 9, last column). This observation might suggest that amine amounts available for nitrosation was not a limiting factor in most engine runs of the duration used.

During method development, the engine was sampled at different times, but an attempt to draw any conclusions from those results were avoided since the engine variables were not controlled. Nitrosamine measurements taken during method development are given in Appendix G.

If we look at the nitrosamine levels of each engine irrespective of NO and NO_2 concentrations (nitrosamines/$NO.NO_2$), it is observed that the nitrosamine amounts produced per $NO.NO_2$ is highest for idle case which corresponds to the lowest crankcase flows. This observation suggests that the time of contact is important and in cases of low flow (and consequently longer contact time cases between the NO_x and the amines in the oil) the nitrosamine levels produced are higher. Thus the nitrosamine levels are probably limited by the contact time.

Usually the nitrosamine amount produced per $NO.NO_2$ is high for the first mode of the engine run which could be attributed to the low flow rates associated with this mode or to carry over from nitrosamines produced during 1 hr engine warm up time.

If we compare the ratios of NDMA/$NO.NO_2$ in different engines using the same oil (namely DDAD, Mack, Caterpillar with Mobil Delvac Super 15-W-40 oil) we will be comparing nitrosamine levels irrespective of $NO.NO_2$ concentrations and oil type (see Tables 3 through 9, last column). The high value of NDMA/$NO.NO_2$ in the Detroit Diesel engine can be explained by the lower crankcase flows all through the modes and higher contact time between the NO_x and the nitrosamine precursors. See Appendix C, Table 6 for flows of heavy duty engines & Table 16 for the crankcase flow of light duty engine.

Comparison of NDMA/$NO.NO_2$ levels in Mack and Caterpillar suggests an engine parameter other than the crankcase flow rates is involved in determining the nitrosamine levels since, the flow rates for these two engines are quite similar. (See Appendix C, Table 6 for flows).

Correlation analysis between the crankcase nitrosamine levels (μg/0.5 hr) and NO_x, NO_2, $(NO_2)^2$, $NO.NO_2$ (the multiple of NO and NO_2), $NO.NO_2/T$ (T = the temperature in degrees Kelvin) were made and correlation coefficients (r) and determination coefficients (r^2) were calculated to obtain a measure of the degree of association between the above variables. In most cases the r values between the nitrosamine levels and $NO.NO_2$ were highest as compared to NO_x, NO_2, NO^2, $NO.NO_2/T$. These r values were around 0.8, 0.9 which indicates a fairly strong linear relationship between the two (see Tables 18 and 19).

The oil analysis procedure developed here is a new concept in nitrosamine analysis. It is efficient, and again has been shown to be artifact free. It should be noted that the recovery rates are affected by a number of factors, for example, when samples were spiked at the 1 ppb level, the recoveries for NDMA were around 50%. Spiking samples the 10 ppb level however, resulted in recoveries as high as 80%. Other experimental conditions such as gas flow rate and the sample temperature also affect the recoveries. For this reason, whenever this method is utilized, the recoveries should be determined for the exact set of conditions used during the analysis.

Most of the used and unused oil samples that were analyzed in the as received condition did not contain any volatile nitrosamines (detection limit NDMA: 0.1 ppb; NMOR: 0.5 ppb in oil.)

After nitrosation by NO_x in the laboratory, most of the oil samples produced NDMA and NMOR indicating that the precursors for these nitrosamines already exist in the oil and in fact NDMA and NMOR were the only two volatile nitrosamines observed in the crankcase emissions. The nitrosation ability did not show any correlation with the nitrogen content of the oil (see Appendix I for nitrogen content of some oils).

The nitrosamine levels obtained by nitrosating certain unused oils can be used to determine the susceptability to nitrosation of those oils in high nitrogen oxide environments such as those found in the crankcases of automobiles and trucks. A high positive correlation of $r = 0.97$, $r^2 = 0.94$ (see Table 17) between the two has been demonstrated for Mack ETAY B 673A engine. The regression line is given in Figure 13. Therefore, for this engine, and under the conditions we performed the testing, given the nitrosation level of a new oil, the NDMA emission rate after one hour of preconditioning can be predicted using the equation $y = 8 + 0.3x$, y being the NDMA in the emissions; X being the nitrosation level of the new oil. It is unknown if this relationship is valid after extended periods of engine operation.

Data from the light duty vehicle also show the presence of nitrosamines in the crankcase emissions and high value of NDMA/NO.NO_2 ratio for this vehicle agrees with the assumption that low crankcase flow rates will produce more nitrosamines per unit NO.NO_2 (See Table 9).

Diesel tailpipe exhaust from a Mack Diesel engine was also collected and analyzed for volatile nitrosamines. The pertinent results are given in Appendix H.

Table 18
Linear Regression Results for NDMA versus $NO.NO_2$

	Mack	Mack	Mack	Mack	Caterpillar	Detroit Diesel	Mack Caterpillar Detroit Diesel
Oil	1	2	3	4	4	4	4
r	0.78	0.80	0.90	0.93	0.72	0.87	0.92
r^2	0.61	0.64	0.81	0.86	0.52	0.76	0.85

Table 19
Linear Regression Results for NMOR versus $NO.NO_2$

	Mack	Mack	Mack	Mack	Caterpillar	Detroit Diesel
Oil	1	2	3	4	4	4
r	-	-	0.85	0.97	0.89	-
r^2	-	-	0.72	0.94	0.79	-

Oil 1 Shell Rotella T SAE 30
2 Amoco 300 SAE 30
3 Mobil Delvac 1200 SAE 30
4 Mobil Delvac Super 45 W 40

- NMOR was not detected

Appendix A

Scope of Work

68-03-2719

Exhibit A
Scope of Work

A. The major objective of this work is to qualify and employ a suitable sampling and analysis methdology in the testing of several heavy duty diesel engines for crankcase emissions of nitrogen compounds such as nitrosamines and nitrosamine precursors. The selection of test engines should be such that a better estimate of the magnitude of the nitrosamine (or precursor) emission problem can be made. In order to achieve these objectives, the following tasks shall be performed.

B. Task 1 - Sampling and Analysis Methodology Qualification

1. There are several crankcase emissions sampling methodologies that have been used in the past. Whereas one or more of these methods may function adequately, none of them have yet been well qualified. Therefore, the contractor, with input from the OMSAPC and ORD Co-Project Officers, shall select the most appropriate such crankcase emissions sampling method, set it up, and qualify its performance. This qualification shall consist of, as a minimum, recovery and blank tests. Recovery tests are considered to be those that prove that if nitrosamines or their precursors are present in the blowby stream that they will indeed be detected. The blank tests are those that confirm that artifact nitrosamines (or precursors) are not being formed by the smapling or sampling handling method. An example of such artifact nitrosamine formation would be the possible formation of n-dimethylnitrosamine from dimethylamine and NOx, in an acidic environment. The major emphasis in the qualification phase will be with n-dimethylnitrosamine and n-diethylnitrosamines. The Project Officer shall approve of the sampling method's performance prior to its use for engine testing.

2. The method used for analyzing the samples that result from both the system qualification phase and engine testing shall have a detection limit no higher than 30 parts per trillion (Vol/vol). Structural evidence of the nitrosamine compounds detected is also required, at a detection limit of 30 parts per billion (Vol/vol). The analytical services can be provided by the Contractor either directly or through a subcontract. This task plus the GC-MS analyses required in Task III should represent about one-half of the total contractual effort.

C. Task II - Engine Selection

The Environmental Protection Agency shall select and provide, or arrange for the engines to be tested. A total of three (3) engines shall be tested.

SCOPE OF WORK

68-03-2719

D. Task III - Engine Testing

The engines shall be operated over a 13 mode schedule. During the 13 mode schedule, measurements will be made of at least NOx and total gaseous blowby rate. Samples shall also be taken for subsequent analysis by the methods described in Task I. The analyses should concentrate on nitrogen containing compounds such as nitrosamines and their precursors. Structural evidence of any nitrosamines detected must be provided. It is understood Engine Testing shall be accomplished by an EPA designated source. The contractor will not do the testing but shall take samples.

Appendix B

Diesel Fuel Analysis for Nitrosamines

Number 2 fuel oil was obtained from the fuel tank of Mack diesel 675. 30 ml of the fuel was extracted with 2 x 5ml 25% Methanol (MeOH) in water (H_2O) in a separatory funnel. MeOH/H_2O layer was poured into a Preptube™ and extracted with 50 ml DCM. DCM was reduced to 1 ml in 55°C waterbath and analyzed on GC-TEA and HPLC-TEA. It showed 9 ppb NDMA on GC and 3 ppb NDMA on HPLC. Whether this could be a likely source of nitrosamines in the crankcase emissions has not been investigated.

Appendix C

Engine Variable Measurements Provided by SWRI

SOUTHWEST RESEARCH INSTITUTE
POST OFFICE DRAWER 28510 • 6220 CULEBRA ROAD • SAN ANTONIO, TEXAS 78284 • (512)684-5111

August 6, 1979

TO: Environmental Protection Agency
Ann Arbor, Michigan 48105

ATTN: Thomas M. Baines
Project Officer

RE: EPA Purchase Order A-0284-NALX
Dated June 1, 1979

SUBJECT: Final Letter Report "Diesel Engine Crankcase Samples and Related Data."

From July 26 to August 3, 1979, several HD Diesel engines and one light-duty Diesel vehicle were operated for the purpose of collecting samples of the crankcase vent gases for DMNA analyses. The sampling for DMNA was carried out by staff (Ulku Goff and Jim Coombs) the New England Institute of Life Sciences while the supplemental data of engine operation, NO, NO$_x$ and NO$_2$ content of the vent gases, 20 x 20 Pallflex filters (Mack engine only) and related items were performed by SwRI. The engines and vehicle were those already at SwRI having been used in previous EPA projects through the courtesy of the respective manufacturers.

It is understood that the data will be used by NEILS in their final report to EPA. Therefore, the data are appended in their most available format. The limited nature of the purchase order precludes any reformatting of already available data. Therefore the use of Xerox copies is considered satisfactory.

In accord with the scope of work for the purchase order, the following items are supplied:

A. HD Diesel Engines

1. Full description of engines
2. 13-mode FTP HC, CO, NO$_x$, BSFC smoke
3. Standards for comparison
4. Crankcase flow rates - 7 modes
5. NO$_2$ and NO concentrations in crankcase vent gases
6. Temperature of the water in/out, engine oil, and crankcase vent gases at point of sample

SAN ANTONIO, HOUSTON, TEXAS, AND WASHINGTON, D.C.

A 20 x 20 size Pallflex filter was taken during the 1900 rpm, 50 percent rated load condition of the Mack engine. The filters have been sealed and stored in the freezer awaiting your shipping instructions. Data for the four filters of the Mack are listed below.

1. Engine Description

The DDAD 6V-71N engine was tested in the 4 valve head configuration with B-60E injectors set at 1.500 timing. These injectors, though certified use in this type engine, were not entered into production as LSN60 injectors were retained. This engine is described on Table 1. It was furnished to SwRI by DDAD in late 1971 and is assumed to be a 1971 model year engine.

Table 2 describes the Mack ETAY(B)673A and the Caterpillar 3406 engines. The Mack was the engine used in the 1000 hour "durability" certification test and is considered a prototype 1975 engine. The Caterpillar engine was the 125 hour "emissions" engine for 1975 EPA certification and is considered a 1975 prototype. The Caterpillar 3406 engine was tested in its indirect injection configuration which features a pre-chamber type combustion system.

2. 13-mode FTP and Federal Smoke

Attached as Tables 3, 4, and 5 are typical 13-mode FTP (pre 1979 test procedure) and cycle weighted BSFC results. Listed below are Federal Smoke results for each engine.

	Opacity, % by EPA meter		
	a	b	c
DDAD 6V-71N	12.3	5.7	25.6
Mack ETAY(B)673A	11.5	11.3	22.5
Caterpillar 3406	11.9	5.4	28.6

3. Standards for Comparison

The only standard in effect for the DDAD 6V-71N engine was the 1970-1973 smoke requirement (Federal Smoke Test) of an "a" factor of 40 percent and "b" factor of 20 percent. For the two 1975 engines (Mack and Caterpillar) the 1974 Federal limits were "a"-20, "b"-15 and "c"-50 percent opacity. The Federal gaseous emissions standards for the two 1975 year Diesel engines were CO 40 grams/bhp-hr (53.6 grams/kw-hr) and HC + NO as NO_2 16 grams/bhp-hr (21.4 grams/kw-hr). California had separate standards for 1975 model years and they were 40.2 grams/kw-hr CO (30 grams/bhp-hr) and HC + NO as NO_2 of 13.4 grams/kw-hr (10 grams/bhp-hr).

4. Crankcase Flow Rates

Table 6 lists the crankcase flow rates measured for the three HD engines. Those were obtained by means of a thin-plate orifice and vacuum source adjusted to give zero psig gage pressure, i.e., source atmospheric, at the crankcase vent.

5. NO-NO_2 Concentrations

Table 7, 8 and 9 lists the modal concentrations of the NO and NO_2 for each of the seven modes tested.

6. Temperatures

Table 7 - 9 also lists the various oil, water and vent gas temperatures requested.

7. 20 x 20 Size Filter Samples

Table 10 lists the filter weights for each of the four 20 x 20 size Pallflex filters taken of the Mack crankcase vent gases. The test condition was the same for each oil, namely 1900 rpm and half load, 161.5 hp. Except for the first run which was curtailed due to an electrical storm, each filter was run for 1 hour. The 20 x 20 filter holder was located between an 8" diameter dilution tunnel and the CVS blower and filtered the entire flow of diluted crankcase vent gases. The nominal CVS blower rate was 85.7 CFM. The dilution level at the 1900/50 percent condition was about 15.2:1.

A practice run on 6/29/79 yielded 2.3574 grams of particulate in a 1 hour test. The filter weights shown in Table 10 vary from 1.86 to 3.48 grams while sampling times varied from 3402 to 3600 seconds. In terms of mg/SCF of flow across the filter, the third run, with Mobil Delvac 1200, Filter PL 45, stands out as being high in weight gain. This filter was reweighed to verify the increase. It was much more oily than the other three runs. No other reason for the increased weight was evident. This was discussed by telecon to Tom Baines on 8/2/79. For comparison, the practice filter has 0.459 mg/SCF on it.

8. Fuel Analyses

Table 11 lists the fuel inspection for the "National Average" No. 2 fuel used in the Mack and Caterpillar engines. This fuel was EM-329-F and is a commercial Gulf 2-D fuel with sulfur content increased to 0.235 percent by weight. Table 12 lists the fuel inspection data for EM-400-F the emissions type 1-D fuel used in the DDAD 6V-71N city bus engine.

Prior to each HD test sequence, the engine was thoroughly preconditioned by running for 30 minutes at intermediate speed and half load and then for 30 minutes at rated speed and half load. Thus, each new oil was run for 1 hour before testing began. A pint sample of used oil was obtained at the conclusion of each test, tagged and furnished to NEILS.

B. Light-Duty

In general, the same type of information was requested for the 1975 Mercedes-Benz 240D Diesel passenger car.

1. Vehicle Description

Table 13 describes the vehicle tested.

2. Tables 14 and 15 are typical 1975 FTP and HFET computer printout sheets using the Emissions 2-D type Diesel fuel.

3. Emissions Standards

This being a 1975 model year car, the standards in effect then were 1.5 g/mile HC (0.9 g/km) 15 g/mile CO (9.3 g/km) and 3.1 g/mile NO_x (1.9 g/km).

4. Crankcase Vent Gas Rate

The crankcase vent rates for the 20 and 50 mph cruise (road load set at 50 mph) are listed on Table 16. Before taking this data, the vehicle was operated for 30 minutes at 40 mph to bring oil and other engine items to stabilized temperature. Shortly after measuring the rates, the 20 mph cruise was run and sampled for 1 hour. The sample at 50 mph was then run also for 1 hour.

5. NO-NO_2 Content in Crankcase Vent Gas

Table 16 lists the NO and NO_2 concentrations in the crankcase vent gases.

6. Temperatures

Table 16 lists water in, out, oil and crankcase vent gas temperature measured.

7. Fuel Analysis

Table 17 lists the inspection results for EM-321-F, the emissions 2-D Diesel fuel used.

This completes EPA P.O. A-0284-NALX. As requested, a copy of this report has been sent to Dr. David Fine at NEILS.

Prepared by:

Karl J. Springer

Karl J. Springer
Director
Department of Emissions Research

cc: Dr. David Fine
New England Institute for Life Sciences
125 Second Avenue
Walthawn, Mass 02154

TABLE 1. DESCRIPTION OF HEAVY DUTY DIESEL ENGINE

Engine Make	Detroit Diesel
Engine Model	6V-71(1)
Engine Serial No.	6VA53347
Strokes/cycle	2
Cylinder Arrangement	V-6
Displacement liters	6.98
cubic inches	426
Compression Ratio	18.7:1
Type Aspiration	Natural Blower Scavenged
Rated Speed, rpm	2100
Power at Rated Speed, kW	163
hp	218
Peak Torque Speed, rpm	1200
Peak Torque, N-M	819
lb-ft	604
Typical Application	City Bus
Typical Fuel Type	DF-1

B-60E injectors at 1.500 timing setting

TABLE 2. DESCRIPTION OF HEAVY-DUTY DIESEL ENGINES

Engine Make	Mack	Caterpillar
Engine Model	ETAY(B)673A	3406 IDI
Engine Serial No.	6F4310	1A5484
Strokes/cycle	4	4
Cylinder Arrangement	I-6	I-6
Displacement, liters	11.01	14.63
cubic inches	672	893
Compression Ratio	14.99	16.5:1
Type Aspiration	TC(a)	TC(a)
Rated Speed, rpm	1900	2100
Power at rated speed, kW	235	242
hp	315	325
Peak Torque Speed, rpm	1450	1400
Peak Torque, N-M	1423.8	1319
lb-ft	1050	970
Typical Application	IC(b)	IC(b)
Typical Fuel Type	DF-2	DF-2

(a) TC-Turbocharged, NA - Naturally Aspirated

(b) IC-Intercity Truck, Tractor, U - Urban Truck and Truck-Tractor

TABLE 3. 13-MODE FEDERAL DIESEL EMISSION CYCLE

DD-AD 6V-71 N COACH ENGINE WITH B-60E INJECTORS 1,500 TIMING
TEST 2 RUN 1 3-24-75 1-D FUEL EM-226-F PROJECT: 11-4016-001

MODE	ENGINE SPEED RPM	TORQUE N X M	POWER KW	FUEL FLOW KG/MIN	AIR FLOW KG/MIN	EXHAUST FLOW KG/MIN	FUEL AIR RATIO
1	440	2,4	,1	,023	4,56	4,58	,005
2	1260	2,4	,3	,063	13,26	13,32	,005
3	1260	185,2	24,4	,123	13,64	13,76	,009
4	1260	375,1	49,5	,203	13,55	13,75	,015
5	1260	557,9	73,6	,283	13,13	13,41	,022
6	1260	740,7	97,7	,393	13,34	13,73	,029
7	440	2,4	,1	,023	4,53	4,55	,005
8	2100	622,0	136,8	,559	21,75	22,31	,026
9	2100	470,0	103,4	,446	21,61	22,06	,021
10	2100	311,0	68,4	,334	21,35	21,68	,016
11	2100	161,4	35,5	,238	21,42	21,66	,011
12	2100	2,4	,5	,151	21,75	21,91	,007
13	440	2,4	,1	,023	4,53	4,55	,005

MODE	HC PPM	CO+ PPM	NO++ PPM	WEIGHTED KW	BSHC G/KW HR	BSCO+ G/KW HR	BSNO2++ G/KW HR	HUM, MILLI G/KG
1	88	107	124	,01	107,20	258,56	495,75	2,1
2	168	254	62	,03	207,97	625,58	249,53	2,1
3	116	158	188	1,95	1,90	5,18	10,10	2,1
4	79	78	355	3,96	,64	1,26	9,39	2,4
5	84	90	649	5,89	,45	,95	11,27	2,4
6	160	1348	988	7,82	,65	10,99	13,22	2,4
7	152	106	124	,01	183,95	256,74	491,26	2,4
8	169	373	780	10,94	,80	3,53	12,12	2,4
9	112	116	529	8,27	,70	1,43	10,74	2,4
10	89	85	280	5,47	,82	1,56	8,47	2,4
11	88	105	150	2,64	1,56	3,72	8,74	2,4
12	236	193	58	,04	288,21	470,49	230,93	2,7
13	188	133	128	,01	227,51	320,77	507,67	2,7

CYCLE COMPOSITE BSHC = 1,238 GRAM/KW HR
BSCO+ = 4,606 GRAM/KW HR
BSNO2++= 11,561 GRAM/KW HR
BSHC + BSNO2++= 12,799 GRAM/KW HR
BSFC = ,290KG/KW HR

+ CONVERTED TO WET BASIS
++ CONVERTED TO WET BASIS AND CORRECTED TO 10,7 MILLIGRAMS WATER PER KG DRY AIR

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TABLE 4. 13-MODE FEDERAL DIESEL EMISSION CYCLE

```
PROJECT : 11-5428-001        DATE 1-8-79     TEST NO. 1
ENGINE  :  MACK ETAY(B)-673A   WITHOUT H2O      APE PUMP
```

MODE	ENGINE SPEED RPM	TORQUE N X M	POWER KW	FUEL FLOW KG/MIN	AIR FLOW KG/MIN	EXHAUST FLOW KG/MIN	FUEL AIR RATIO
1	650	0.0	0.0	.017	3.84	3.86	.005
2	1450	30.4	4.7	.024	9.63	9.70	.008
3	1450	334.5	51.5	.216	10.76	10.98	.020
4	1450	686.1	104.2	.385	13.84	14.22	.028
5	1450	1046.9	158.9	.571	17.20	17.85	.033
6	1450	1391.1	211.2	.773	21.01	21.78	.037
7	650	0.0	0.0	.017	3.89	3.91	.004
8	1900	1175.1	233.8	.927	27.67	28.60	.033
9	1900	890.2	177.1	.680	23.56	24.24	.029
10	1900	605.3	120.4	.475	19.56	20.03	.024
11	1900	306.2	60.9	.279	15.60	15.88	.018
12	1900	33.2	6.6	.117	12.82	12.94	.009
13	650	0.0	0.0	.017	3.94	3.96	.004

MODE	HC PPM	CO+ PPM	NO++ PPM	WEIGHTED KW	BSHC G/KW HR	BSCO+ G/KW HR	BSNO2++ G/KW HR	HUM. MILLI G/KG
1	164	254	256	0.00	R	R	R	4.4
2	264	226	243	.37	15.91	27.10	47.94	4.4
3	231	137	541	4.12	1.43	1.69	10.98	4.4
4	149	129	887	8.33	.79	1.02	11.54	4.4
5	94	226	1061	12.72	.31	1.47	11.35	4.4
6	64	340	1109	16.40	.19	2.03	10.89	4.4
7	154	136	284	0.00	R	R	R	4.4
8	66	258	722	18.70	.23	1.83	8.42	4.4
9	114	173	623	14.17	.45	1.37	8.13	4.4
10	176	113	440	9.63	.85	1.14	6.97	4.4
11	206	149	264	4.87	1.56	2.26	6.54	4.4
12	263	180	141	.53	14.97	20.45	26.34	4.4
13	164	182	219	0.00	R	R	R	4.4

```
CYCLE COMPOSITE    BSHC    =    .707   GRAM/KW  HR
                   BSCO+   =   1.924   GRAM/KW  HR
                   BSNO2++=   9.875   GRAM/KW  HR
            BSHC + BSNO2++=  10.582   GRAM/KW  HR
                   BSFC    =    .241KG/KW HR
```

+ CONVERTED TO WET BASIS

++ CONVERTED TO WET BASIS AND CORRECTED TO 10.7 MILLIGRAMS WATER PER KG DRY AIR

TABLE 5. 13-MODE FEDERAL DIESEL EMISSION CYCLE

PROJECT: 11-4623-001 TEST DATE 4-12-78 TEST NO.1
ENGINE: CATERPILLAR 3406 INDIRECT INJECTION FUEL EM-329-F

MODE	ENGINE SPEED RPM	TORQUE N X M	POWER KW	FUEL FLOW KG/MIN	AIR FLOW KG/MIN	EXHAUST FLOW KG/MIN	FUEL AIR RATIO
1	600	0.0	0.0	.026	4.23	4.26	.006
2	1400	26.1	3.8	.097	10.00	10.10	.010
3	1400	334.7	49.1	.228	10.36	10.59	.022
4	1400	667.1	97.8	.389	11.91	12.30	.033
5	1400	1001.8	146.9	.586	14.66	15.25	.040
6	1400	1343.6	197.0	.809	17.28	18.09	.047
7	600	0.0	0.0	.026	4.76	4.79	.005
8	2100	1113.4	244.8	1.037	24.41	25.44	.042
9	2100	840.4	184.8	.777	20.62	21.40	.038
10	2100	560.2	123.2	.541	16.75	17.29	.032
11	2100	280.1	61.6	.337	14.65	14.99	.023
12	2100	19.0	4.2	.177	13.83	14.01	.013
13	600	0.0	0.0	.031	4.76	4.79	.007

MODE	HC PPM	CO+ PPM	NO++ PPM	WEIGHTED KW	BSHC G/KW HR	BSCO+ G/KW HR	BSNO2++ G/KW HR	HUM. MILLI G/KG
1	120	411	63	0.00	R	R	R	6.2
2	148	464	63	.31	11.36	70.96	15.73	6.2
3	56	173	435	3.93	.35	2.17	8.94	6.2
4	28	114	517	7.82	.10	.83	6.19	6.2
5	12	194	582	11.75	.04	1.17	5.75	6.2
6	6	377	626	15.76	.02	2.01	5.47	6.6
7	68	496	83	0.00	R	R	R	6.6
8	24	166	735	19.59	.07	1.00	7.27	6.6
9	40	140	611	14.78	.13	.94	6.74	6.7
10	12	85	517	9.86	.05	.69	6.91	6.4
11	28	116	423	4.93	.20	1.64	9.80	6.4
12	60	292	118	.33	5.06	56.82	37.80	6.4
13	96	382	45	0.00	R	R	R	6.4

CYCLE COMPOSITE
BSHC = .176 GRAM/KW HR
BSCO+ = 1.939 GRAM/KW HR
BSNO2++= 6.950 GRAM/KW HR
BSHC + BSNO2++= 7.126 GRAM/KW HR
BSFC = .272KG/KW HR

+ CONVERTED TO WET BASIS
++ CONVERTED TO WET BASIS AND CORRECTED TO 10.7 MILLIGRAMS WATER PER KG DRY AIR

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TABLE 6. ENGINE CRANKCASE VENT RATES

Test Mode	1	2	3	4	5	6	7
Speed		Intermediate		Idle		Rated	
Load, %	2	50	100	-	100	50	2

DDAD 6V-71N

	1	2	3	4	5	6	7
Speed, rpm	1260	1260	1260	400	2100	2100	2100
Power, hp obs	3.8	66.4	132.7	---	190.4	95.2	3.5
Flow, lbs/hr	4.01	3.90	4.03	1.61	10.42	9.31	8.04
SCFM	0.89	0.87	0.90	0.36	2.32	2.07	1.79
m^3/min	0.02	0.02	0.02	0.01	0.15	0.06	0.05
m^3/30 min	0.6	0.6	0.6	0.3	4.5	1.8	1.5

Mack ETAY (B)673A

	1	2	3	4	5	6	7
Speed, rpm	1450	1450	1450	600	1900	1900	1900
Power, hp obs	6.3	139.7	283.2	---	313.5	161.5	8.9
Flow, lbs/hr	10.71	19.5	31.8	7.66	43.77	25.35	12.9
SCFM	2.38	4.34	7.08	1.70	9.74	5.63	2.87
m^3/min	0.07	0.12	0.20	0.05	0.28	0.16	0.08
m^3/30 min	2.1	3.6	6.0	1.50	8.4	4.8	2.4

Caterpillar 3406 IDI

	1	2	3	4	5	6	7
Speed, rpm	1400	1400	1400	600	2100	2100	2100
Power, hp obs	5.1	133.9	268.3	---	327.6	163.8	7.0
Flow, lbs/hr	13.10	19.10	30.89	14.91	29.44	24.12	18.48
SCFM	2.91	4.25	6.87	3.32	6.55	5.37	4.11
m^3/min	0.082	0.12	0.19	0.09	0.18	0.15	0.12
m^3/30 min	2.5	3.6	5.8	2.7	5.4	4.5	3.6

TABLE 7. ENGINE TEMPERATURES AND CRANKCASE GAS NO-NO_2 READINGS
Mack ETAY(B)673A

Test Mode	1	2	3	4	5	6	7
Speed	Intermediate			Idle	Rated		
Load, %	2	50	100	-	100	50	2
Speed RPM	1450	1450	1450	600	1900	1900	1900
Power, hp obs	6.3	139.7	283.2	---	313.5	161.5	8.9
Shell Rotella T 30 wt Em-296-EO, 7/26/79							
Temps °F oil	186	198	208	174	215	201	190
water in	180	174	172	179	173	174	179
water out	181	178	183	179	184	182	178
crankcase	162	180	219	172	226	198	165
NO,ppm	22.5	75.3	114.6	17.1	127.5	100.2	33.4
NO_2 ppm	3.0	69.3	74.1	4.0	109.8	33.6	6.1
Amoco 300 30 wt EM-392-EO-A, 7/27/79							
Temps °F oil	185	196	206	171	213	200	188
water in	181	178	178	179	175	174	177
water out	181	181	182	180	185	183	178
crankcase	161	180	212	154	224	191	161
NO, ppm	25.3	101.4	132.6	13.8	123.3	69.6	31.0
NO_2, ppm	4.1	69.9	88.8	1.9	86.7	72.6	7.5
Mobil Delvac 1200 30 wt EM-398-EO; 7/30/79							
Temps °F oil	185	195	206	173	213	201	189
water in	178	173	175	180	173	174	174
water out	180	181	182	180	184	182	176
crankcase	161	177	210	169	223	195	165
NO, ppm	22.5	105.3	114.0	20.5	123.3	84.0	29.4
NO_2, ppm	9.7	69.9	64.8	3.7	97.2	54.6	6.2
Mobil Delvac Super 15W40 EM-399-EO, 7/31/79							
Temps °F oil	185	195	208	175	214	203	189
water in	178	173	171	179	172	178	174
water out	179	182	183	180	183	181	179
crankcase	161	178	212	173	220	197	165
NO, ppm	23.3	90.3	144.6	21.6	128.1	101.7	26.4
NO_2, ppm	3.3	59.4	91.5	4.5	117.9	41.1	10.3

TABLE 8. ENGINE TEMPERATURES AND CRANKCASE GAS NO-NO_2 READINGS

Detroit Diesel 6V-71N B60E

Mobile Delvac Super 15W40, EM-399-EO 8/1/79

Test Mode	1	2	3	4	5	6	7
Speed		Intermediate		Idle		Rated	
Load, %	2	50	100	---	100	50	2
Speed, rpm	1260	1260	1260	400	2100	2100	2100
Power, hp ohs	3.8	66.4	132.7	---	190.4	95.2	3.5
Temps °F oil	183	196	216	177	216	204	196
water in	165	164	186	169	166	166	166
water out	172	177	166	172	184	178	175
crankcase	155	160	171	143	190	183	178
NO, ppm	2.4	4.3	11.4	7.3	19.3	5.5	1.7
NO_2, ppm	1.3	0.4	1.0	0.5	1.0	0.9	0.7

TABLE 9. ENGINE TEMPERATURES AND CRANKCASE GAS NO-NO_2 READINGS

Caterpillar 3406 IDI PC

Mobil Delvac Super 15W40, EM-399-EO 8/2/79

Test Mode	1	2	3	4	5	6	7
Speed		Intermediate		Idle		Rated	
Load, %	2	50	100	---	100	50	2
Speed, rpm	1400	1400	1400	600	2100	2100	2100
Power, hp ohs	5.1	133.9	268.3	---	327.6	163.8	7.0
Temps °F oil	183	197	215	174	225	212	200
water in	161	162	164	161	164	163	162
water out	169	178	192	168	190	179	172
crankcase	152	173	217	163	227	198	168
NO, ppm	6.9	24.5	20.6	4.2	54.9	35.4	37.0
NO_2, ppm	0.4	2.1	4.3	0.4	9.3	3.3	0

TABLE 10. 20 x 20 Filter Data - MACK ETAY(B)673A

Oil Code EM-	396-EO	397-EO-A	398-EO	399-EO
Oil Description	Shell Rotella T	Amoco 300	Mobil Delvac 1200	Mobil Delvac Super
SAE Wgt.	30	30	30	15W40
Filter Number (SwRI)	PL-43	PL-44	PL-45	PL-47
EPA Filter Code CABS-79-	0240	0250	0260	0270
Filter Weight, grams	1.8593	2.2231	3.4825	2.3427
Sample Time, sec	3402	3600	3600	3600
Diluted flow across filter, SCF	4732	5072	5106	5073
Rate, mg/SCF	0.393	0.438	0.682	0.462

TABLE 12. EMISSIONS 1-D

HOWELL HYDROCARBONS
San Antonio, Texas
LABORATORY REPORT

EM-400 F
TANK 8

Sample: TK 99 Type I Diesel

Date: 6-19-79

INSPECTION	
Gravity, °API	42.9
Color	
Doctor	
Corrosion	
R V P	
Octane No. F-1 Clear	
Octane No. F-1 + ____ ml TEL	
Octane No. F-2 Clear	
Octane No. F-2 + ____ ml TEL	
Total Sulfur, Wt. %	.18
Mercaptan Sulfur	
Flash, F.	+ 140°

DISTILLATION			
	% @	Initial Boiling Point	374
	% @	5%	392
	% @	10%	398
	% @	20%	404
	% @	30%	408
	% @	40%	414
	% @	50%	418
		60%	422
		70%	429
		80%	440
		90%	461
		95%	496
		End Point	560
		Recovery	99.0
		Residue	1.0
		Loss	

Pour Point, F.		Diesel Index		Paraffins, %	
Cloud Point, F.		Cetane No.	49.0	Olefins, %	
Freeze Point, F.		Viscosity, S S @____ F.		Naphthenes, %	
Smoke Point, mm		Viscosity, @ 100 F.	1.7	Aromatics, %	16.2
Aniline Point, °F.		B.S. & W.			
Aniline Gravity Const.		A.S.T.M. Existent Gum, mg.			
Water Tolerance		Potential Gum, mg.			

Remarks:

Tested By: Tim S. McLeod, Chief Chemist

TABLE 13. DESCRIPTION OF TEST VEHICLES

Vehicle Model	Mercedes 240D
Engine Model (if different)	OM616
V.I.N.	11511710066208
Engine No. (if different)	616916-10-052895
Body Type	4 door sedan
Loaded Weight, kg (lb_m)[a]	1492 (3289)
Inertia Equivalent, kg (lb_m)	1588 (3500)
Transmission	4 speed manual
Displacement, ℓ(in^3)	2.40 (146.7)
Cylinders	4
Power, kW (hp) @ rpm	46.2 (62) @ 4350
Injection System	Bosch
Combustion Chamber	prechamber
Compression Ratio	21.0
Distance on Vehicle, km[b]	7182

[a] curb weight plus 136 kg (300 lb_m)

[b] at end of project

```
                              TABLE 14              VEHICLE EMISSION RESULTS
                               1975  LIGHT DUTY EMISSIONS TEST

UNIT NO.  ???          TEST NO. 5          DATE  3/16/77                         MFGR. CODE   -0
VEHICLE MODEL  MERCEDES DIESEL             ENGINE   2.41 LITRE 6 CYL.            TEST WT.  1587 KG                YR. 1975
TEST TYPE  240-D                           COMMENTS  1975 FTP 3 BAG EM-238-F                                      ROAD LOAD    8.4 KW

BAROMETER 744.22 MM OF HG.
DRY BULB TEMP.    23.9 DEG. C                                             WET BULB TEMP  16.1 DEG. C
REL. HUMIDITY      44 PCT.                                                 ABS. HUMIDITY   8.3 MILLIGRAMS/KG
EXHAUST EMISSIONS

    BLOWER DIF. PRESS., G2, 469.9 MM. H2O                                 BLOWER INLET PRESS., G1 406.4 MM. H2O
                                                                          BLOWER INLET TEMP.    43 DEG. C
    BAG RESULTS
    BAG NO.                                          1             2             3
    BLOWER REVOLUTIONS                            9129         15697          9125
    HC    SAMPLE  METER READING/SCALE            4.8/4        11.9/2        11.4/2
    HC    SAMPLE  PPM                               39            24            23
    HC    BACKGRD METER READING/SCALE            6.2/2         5.8/2         6.2/2
    HC    BACKGRD PPM                               12            12            12
    CO    SAMPLE  METER READING/SCALE           46.9/*        32.6/*        39.2/*
    CO    SAMPLE  PPM                               44            30            37
    CO    BACKGRD METER READING/SCALE            1.2/*         1.7/*         1.2/*
    CO    BACKGRD PPM                                1             2             1
    CO2   SAMPLE  METER READING/SCALE           62.9/3        42.6/3        55.6/3
    CO2   SAMPLE  PERCENT                         1.12           .73           .98
    CO2   BACKGRD METER READING/SCALE            3.1/3         4.3/3         2.9/3
    CO2   BACKGRD PERCENT                          .05           .07           .04
    NOX   SAMPLE  METER READING/SCALE           37.1/2        25.1/2        35.0/2
    NOX   SAMPLE  PPM                             37.1          25.1          35.0
    NOX   BACKGRD METER READING/SCALE             .6/2          .6/2          .6/2
    NOX   BACKGRD PPM                               .6            .6            .6

    HC    CONCENTRATION PPM                         27            13            11
    CO    CONCENTRATION PPM                         42            28            34
    CO2   CONCENTRATION PCT                       1.08           .66           .93
    NOX   CONCENTRATION PPM                       36.6          24.5          34.4
    HC    MASS GRAMS                              1.08           .87           .45
    CO    MASS GRAMS                              3.34          3.87          2.76
    CO2   MASS GRAMS                           1368.39       1444.83       1186.97
    NOX   MASS GRAMS                              4.48          5.17          4.22
     HC    MASS MG                                1.08           .87           .45

    WEIGHTED MASS HC          .13 GRAMS/KILOMETRE
    WEIGHTED MASS CO          .57 GRAMS/KILOMETRE
    WEIGHTED MASS CO2      224.47 GRAMS/KILOMETRE
    WEIGHTED MASS NOX         .74 GRAMS/KILOMETRE

  CARBON BALANCE FUEL CONSUMPTION =  8.42 LITRES PER HUNDRED KILOMETRES
  TOTAL CVS FLOW =   256.9 STD. CU. METRES
```

```
       TABLE 15.     EXHAUST EMISSIONS FROM SINGLE BAG SAMPLE
                              VEHICLE NUMBER

DATE  3/16/77                TIME    -0 HRS.         TEST NO.  5
MODEL  1975 MERCEDES DIES. FET                       ENGINE 2.4 LITRE    6 CYL.
DRIVER   DT                  TEST WT.  1587 KG.      GVW    0 KG
WET BULB TEMP  17 C          DRY BULB TEMP  24 C     REL. HUM.  45.0 PCT
SPEC. HUM.   8.8 GRAM/KG     BARO.  742.7 MM  HG.    MEASURED FUEL  0.00 KG
DISTANCE  16.476 KM          FUEL 847.3 G/LITRE   FUEL HC  RATIO 1.844

  RUN DURATION          12.78 MINUTES
  BLOWER INLET PRESS. 393.7  MM. H2O
  BLOWER DIF.  PRESS. 457.2  MM  H2O
  BLOWER INLET TEMP.     50  DEG. C
  DYNO REVOLUTIONS    23549
  BLOWER REVOLUTIONS    13835
  BLOWER CU. CM /REV.  8707

  BAG RESULTS
   HC   SAMPLE  METER READING/SCALE             11.0/2
   HC   SAMPLE  PPM                               22
   HC   BACKGRD METER READING/SCALE              2.9/2
   HC   BACKGRD PPM                                6
   CO   SAMPLE  METER READING/SCALE             59.6/*
   CO   SAMPLE  PPM                               57
   CO   BACKGRD METER READING/SCALE              8.1/*
   CO   BACKGRD PPM                                8
   CO2  SAMPLE  METER READING/SCALE             83.6/3
   CO2  SAMPLE  PERCENT                         1.54
   CO2  BACKGRD METER READING/SCALE              3.1/3
   CO2  BACKGRD PERCENT                          .05
   NOX  SAMPLE  METER READING/SCALE             61.1/2
   NOX  SAMPLE  PPM                             61.1
   NOX  BACKGRD METER READING/SCALE               .7/2
   NOX  BACKGRD PPM                               .7
   HC   CONCENTRATION PPM                         17
   CO   CONCENTRATION PPM                         48
   CO2  CONCENTRATION PCT                       1.50
   NOX  CONCENTRATION PPM                       60.5
   SO2  CCCENTRATION PPM                         0.0
   HC   MASS (GRAMS)                            1.00
   CO   MASS (GRAMS)                            5.72
   CO2  MASS (GRAMS)                         2835.77
   NOX  MASS (GRAMS)                           11.16
   SO2  MASS (GRAMS)                            0.00

HC   GRAMS/KILOMETRE       .06
CO   GRAMS/KILOMETRE       .35
CO2  GRAMS/KILOMETRE    172
NOX  GRAMS/KILOMETRE       .68
SO2  GRAMS/KILOMETRE      0.00

HC   GRAMS/KG OF FUEL   1.11     HC   GRAMS/MIN        .1
CO   GRAMS/KG OF FUEL    6.4     CO   GRAMS/MIN       .4
CO2  GRAMS/KG OF FUEL   3160     CO2  GRAMS/MIN     222
NOX  GRAMS/KG OF FUEL  12.43     NOX  GRAMS/MIN     .87
SO2  GRAMS/KG OF FUEL   0.00     SO2  GRAMS/MIN    0.00

CARBON BALANCE FUEL CONSUMPTION =  6.43 LITRES PER HUNDRED KILOMETRES
```

TABLE 16. MERCEDES-BENZ 240D CRANKCASE DATA
Mobil DELVAC SUPER 15W40, 8/3/79

Vehicle speed, mph	20	50
Vehicle HP, indicated	1.4	9.9
actual		11.2
Flow, lbs/hr	3.85	5.35
SCFM	0.86	1.19
m^3/min.	0.025	0.035
m^3/30 min.	0.75	1.04
Temps. °F oil	189	234
water in	87	169
water out	173	187
crankcase	121	151
NO, ppm	6.2	8.0
NO_2, ppm	0.4	0.6

Inertia - 3500 lbs

1 lb/hr = 0.0065 m^3/min.

TABLE 17. EMISSIONS 2-D Fuel

MEMORANDUM

TO: All who use Emissions 2D fuel

FROM: Karl J. Springer KJS

DATE: March 20, 1978

The latest batch of Howell 2D Diesel Emissions fuel is coded EM-321-F and is in Tanks 5 & 6. The inspection data is shown below. This fuel is in use effective on its delivery of about 3/15/78.

cc:C. T. Hare
O. J. Davis
S. F. Martin
T. L. Ullman
J. G. Chessher
V. Markworth
R. Hull

Sample TK 105 Type #2 Diesel	Date 3-10-78

INSPECTION	
Gravity, °API	36.9
Color	NPA1½
Doctor	
Corrosion	1A
R V P	
Octane No. F-1 Clear	
Octane No. F-1 + ____ ml TEL	
Octane No. F-2 Clear	
Octane No. F-2 + ____ ml TEL	
Total Sulfur, Wt. %	.29
Mercaptan Sulfur	
Flash, F.	155°

DISTILLATION			
	%@	Initial Boiling Point	382
	%@	5%	400
	%@	10%	408
	%@	20%	428
	%@	30%	448
	%@	40%	458
	%@	50%	488
		60%	509
		70%	528
		80%	550
		90%	582
		95%	615
		End Point	650
		Recovery	99.0
		Residue	1.0
		Loss	0.0

Pour Point, F.	+20	Diesel Index		Paraffins, %	
Cloud Point, F.	+25	Cetane No.		Olefins, %	
Freeze Point, F.		Viscosity, SUS @ 100 F.	34.0	Naphthenes, %	
Smoke Point, mm		Viscosity, KV @ 100 F.	2.40	Aromatics, %	30.5
Aniline Point, °F.		B.S. & W.			
Aniline Gravity Const.		A.S.T.M. Existent Gum, mg.			
Water Tolerance		Potential Gum, mg.			

Remarks:

Tested By: Torry C. Tomblin, Chief Chemist

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Appendix D

Comparison of GC-TEA and GC-MS Results

Confirmation of NDMA on GC-TEA and GC-MS.

Sample No.	Engine	Oil	GC-TEA (ppm)	GC-MS (ppm)
1	Mack ETAY (B) 673A	Mobil Delvac Super 15 W 40	5.1	5
2	Mack ETAY (B) 673A	Mobil Delvac 1200	4.9	5
3	Caterpillar 3406	Mobil Delvac Super 15 W 40	1.9	2
4	DDAD 6V-71N	Mobil Delvac Super 15 W 40	1.6	1
5	Mack ETAY (B) 673A	Amoco 300 SAE30	1.4	1.5

LABORATORY OF THE GOVERNMENT CHEMIST D-3
Cornwall House, Stamford Street, LONDON S.E.1
Telephone: **01-928 7900, ext.** 625

Please address any reply to
THE GOVERNMENT CHEMIST
and quote:
Your reference:

14 December 1979

Dear Dr. Goff,

With reference to your letter of 13 November 1979, I am sorry that I have been so long in replying however I list below the information that you require:-

Results of analysis by GC-high resolution MS:-

Sample 1	NDMA	5 ppm
Sample 2	NDMA	5 ppm
Sample 3	NDMA	2 ppm
Sample 4	NDMA	1 ppm
Sample 5	NDMA	1.5 ppm

The instruments used were a Kratos-AEI MS902 mass spectrometer operated in the peak matching mode and coupled to a Pye 104 gas chromatograph using a silicone rubber membrane separator.

The conditions of analysis were as follows:-

Gas Chromatograph:-

Carrier gas	Helium	
Flow rate	15 ml/min	
Temperatures	Injection port	170°C
	Column	160°C
	Separator	160°C
	Transfer line	160°C

Column 10 ft x 1/8 inch stainless steel, 5% Carbowax 20M on 80-100 BS mesh acid washed Chromosorb W.

Sample size 5µl

Mass Spectrometer:-

Accelerating voltage	8 kV
Trap current	100 µA
Electron beam voltage (EI mode)	60 eV (tuned for maximum monitor response)
Multiplier voltage	-2.8 kV
Ion source pressure	3×10^{-6} torr
Resolution (10% valley)	7000

A fuller discussion of this type of procedure is given in J. Chromatogr. 64, 201-210 (1972) by T A Gough and K S Webb.

If any of these points require further clarification please do not hesitate to contact me.

Yours faithfully,

Kenneth S. Webb

Figure Captions:

Figure 14	GC-TEA analysis of the combined extracts that were confirmed on GC-MS.
Figure 14-a	4 ng NDMA standard
Figure 14-b	Sample 1, showing the presence of 5.1 ppm NDMA in solution.
Figure 14-c	Sample 2, showing the presence of 4.9 ppm NDMA in solution.
Figure 14-d	Sample 3, showing the presence of 1.9 ppm NDMA in solution.
Figure 14-e	Sample 4, showing the presence of 1.6 ppm NDMA in solution.
Figure 14-f	Sample 5, showing the presence of 1.4 ppm NDMA in solution.

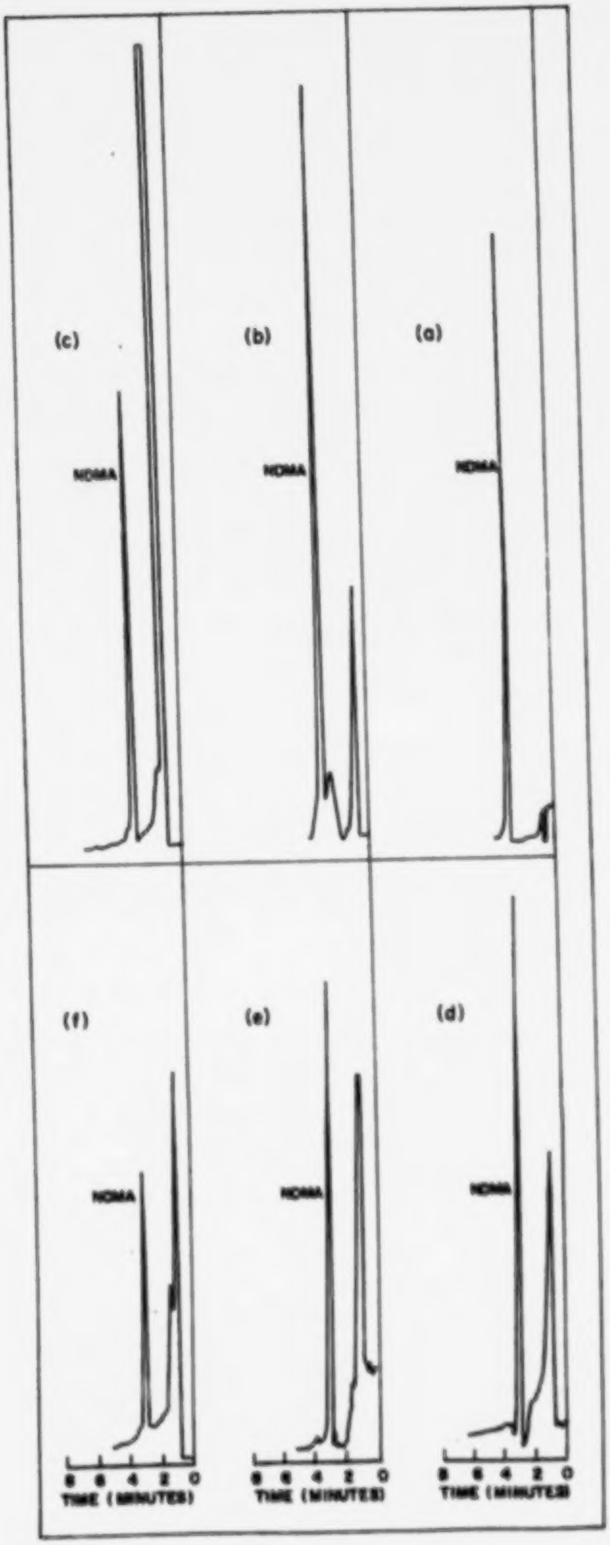
(c)
(b)
(a)
NDMA
NDMA
NDMA
(f)
(e)
(d)
NDMA
NDMA
NDMA
8 6 4 2 0
TIME (MINUTES)
8 6 4 2 0
TIME (MINUTES)
8 6 4 2 0
TIME (MINUTES)

Figure: 14

Appendix E

The Information Supplied by Various Engine Manufacturing and Oil Companies

E-2

Volume 63 Number 2 1977

Lubrication

A Technical Publication Devoted to the Selection and Use of Lubricants

PUBLISHED BY
TEXACO INC.
TEXACO PETROLEUM PRODUCTS

LUBRICATION

A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

Published by
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R. F. Meeker, Editor

FUEL AND LUBRICANT ADDITIVES—II

LUBRICANT ADDITIVES

George J. Schilling and Gordon S. Bright

The previous issue of this publication[16] presented the function of and cited examples of typical chemical additives commonly used in gasoline, and in middle distillate and residual fuels. This issue concludes the article with a general discussion of lubricant additives, and then presents a detailed description of the additives typical of those used in automotive drive-train and industrial lubricants.

As emphasized in the previous issue, additives cited in this article are examples only. Their mention in this context is exemplary and illustrative, and is not intended to imply that any particular additive or additive package is used in any specific commercial automotive or industrial lubricant, and should not be inferred.

The term "additive" is used in this issue to cover those materials added to a lubricant to impart or enhance desirable properties, or to eliminate or minimize deleterious properties. A lubricant can be defined as a gas, liquid, or solid capable of reducing friction, heat, and wear when introduced between two solid surfaces in relative motion. Mineral oils refined from crude oil provided satisfactory liquid lubricants for machinery for many years, but most modern equipment demands more from a lubricant than mineral oils alone can provide. A variety of additives has been developed to improve the properties of mineral oils, and to give them desirable new properties. The trend to higher operating temperatures in automotive drive-trains, the imposition of engine emission controls, and optimum industrial production are reasons for the development of better lubricants and a steady increase in additive production[17], as indicated by Figure 16.

Lubricant additives can be grouped into three main functional areas: those which protect the lubricated surfaces, those which improve lubricant performance, and those which protect the lubricant itself.[18] The relationship between additive types and their functions is general, and can be applied to lubricants for engines, transmissions and rear axles in automobiles, trucks, off-highway equipment, and a wide variety of industrial equipment. The formulation of a lubricant for a specific application is a difficult task which requires identification of performance needs, knowledge of the additives that meet those needs, and finally, careful selection of the appropriate base oils and additives.

Many types of additives perform more than one function. For example, zinc dithiophosphates protect metal surfaces from wear and corrosion. They also protect the lubricant from decomposition by preventing the oxidation processes that lead to the formation of corrosive acids and deposit precursors. Thus, in this instance, the additive is multifunctional.

One very important point must be made. In

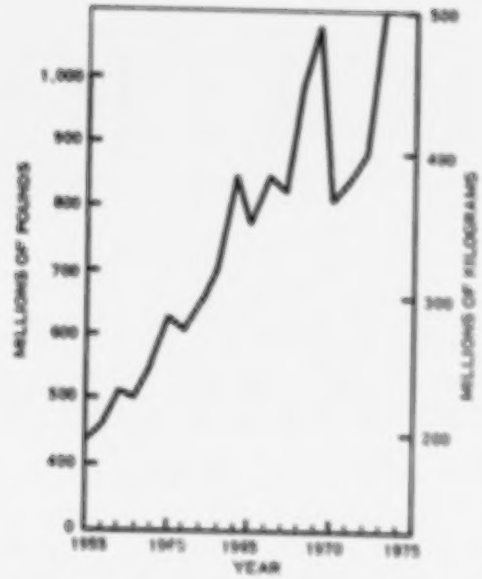


Figure 16 — Lubricant additive production in the United States, 1955-1975.

choosing additives for any product, whether it be a liquid lubricant or a grease, it must be borne in mind that the effectiveness of an additive may vary, depending upon the system in which it is used. This is referred to as "additive response." An oxidation inhibitor, for example, that gives excellent results in one base oil may not be as equally satisfactory in another. An EP agent (an additive material which imparts to a lubricant the ability to prevent scuffing of the metallic bearing or gear surfaces under conditions of extreme pressure) that gives high EP characteristics in one formulation may not necessarily give a similar response in a different formulation. Additive response is controlled individually by the various components of the formulation in which they are used, and collectively by the sum of all the individual components. It is also true that this final collective response may be different from the algebraic sum of responses of the individual components. Those cases where the response is greater than would be expected from the known responses of individual components are sometimes referred to as additive synergism.

One further note is needed. The optimum level of additive dosage may differ for different systems. In some cases, an additive may be most effective at a very low dosage and the effectiveness may decrease as the dosage is increased. In other cases, the effectiveness may continue to increase as the amount of additive is increased, or there may be a true optimum dosage.

AUTOMOTIVE DRIVE-TRAIN LUBRICANT ADDITIVES

As mentioned in the introductory section, lubricant additives can be classified as those which (1) protect the lubricated surface, (2) improve lubricant performance, and (3) protect the lubricant. Each of the classifications is discussed as it applies to automotive drive-train lubricant additives.

Surface Protective Additives

Examples of those additives are listed in Table I.

Antiwear and EP Agents

One of the primary functions of a lubricant is to reduce wear. Wear can result from a number of different processes, such as corrosion, metal-to-metal contact, or abrasion by solid particles. Corrosive wear is a particular problem in engines, because the lubricant is likely to be contaminated with moisture and acidic products of combustion[19]. Mechanical wear from metal-to-metal contact or abrasives is normally prevented by hydrodynamic lubrication with an oil film thick enough to keep moving parts separated. Adverse operating conditions such as high load, low speed, and low lubricant viscosity reduce the thickness of the lubricant film to a state referred to as boundary lubrication, where the lubricant film can actually rupture and allow metal-to-metal contact[20,21]. This condition may exist between the piston ring and cylinder wall, the cam and valve lifter, the rocker arm and valve tip inter-

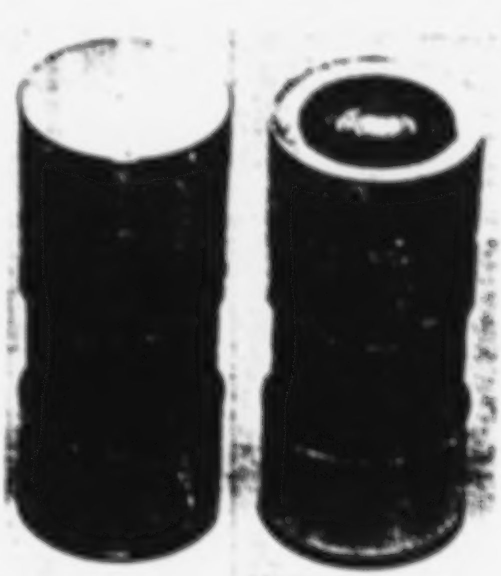


Figure 17 — Valve lifter wear.

TABLE I

SURFACE PROTECTIVE ADDITIVES AUTOMOTIVE LUBRICANTS

Additive Type	Purpose	Typical Compounds	Functions
Antiwear and EP Agent	Reduce friction and wear and prevent scoring and seizure	Zinc dithiophosphates, organic phosphates, and acid phosphates, organic sulfur and chlorine compounds, sulfurized fats, sulfides and disulfides	Chemical reaction with metal surface to form a film with lower shear strength than the metal, thereby preventing metal to metal contact
Corrosion and Rust Inhibitor	Prevent corrosion and rusting of metal parts in contact with the lubricant	Zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines	Preferential adsorption of polar constituent on metal surface to provide a protective film and/or neutralization of corrosive acids
Detergent	Keep surfaces free of deposits	Metallo-organic compounds of barium, calcium and magnesium phenolates, phosphates and sulfonates	Chemical reaction with sludge and varnish precursors to neutralize them and keep them soluble
Dispersant	Keep insoluble contaminants dispersed in the lubricant	Polymeric alkylthiophosphonates and alkylsuccinimides	Contaminants are bonded by polar attraction to dispersant molecules, prevented from agglomerating and kept in suspension due to solubility of dispersant
Friction Modifier	Alter coefficient of friction	Organic fatty acids and amines, lard oil, high molecular weight organic phosphorus and phosphoric acid esters	Preferential adsorption of surface active materials

faces in engines, and between gears in transmissions and rear axles. In these areas, wear may appear as a gradual polishing of the metal surfaces, or as scuffing or spalling[22]. The right hand portion of Figure 17 illustrates severe wear on a valve lifter. Zinc dithiophosphates have enjoyed wide acceptance as antiwear additives in automotive lubricants.

Severe boundary lubrication conditions can develop between the gear teeth in hypoid gear sets, and the gears in the transmissions and axles of heavy equipment[23]. Additives such as alkylpolysulfides, tricresylphosphate or chlorinated organic compounds are used under these conditions and are referred to as EP additives.

Both antiwear and EP additives prevent metal-to-metal contact between parts by forming a coating that will yield under the shear stress imposed during boundary lubrication[19]. Heat from friction between mating surfaces provides energy for the chemical reaction between the additive and metal surfaces that results in the protective coating. Some additives require more energy to react than others, and unless sufficient energy is available, the coating cannot form. The coating may be an iron sulfide, iron phosphate, or some other metallo-organic compound, depending on the particular metal and additive present.

Corrosion and Rust Inhibitors

Corrosion is a chemical attack on metal surfaces, and rust is a specific type of corrosion involving ferrous metals. Corrosive materials contaminate drive-train lubricants in a variety of ways. Lubricants may oxidize in service to form organic acids. The process of combustion introduces moisture and a variety of organic and mineral acids into engine crankcase oils[18,24]. Transmissions and gear cases may ingest moisture from the atmosphere through their vents as they cool after shutdown. Moisture contamination can also react with some EP additives, hydrolyzing them to form acids. The chemically reactive nature of some EP additives can also make them corrosive.

The additives used to prevent corrosion in automotive equipment contain polar functional groups that permit them to preferentially adsorb on metal surfaces. This provides a barrier to prevent corrosive materials from contacting the metallic surfaces. Zinc dithiophosphates and dithiocarbamates are commonly used to protect copper-lead bearings from the type of corrosion illustrated in Figure 18. Rust inhibitors derived from sulfonates and amines also form adsorbed films on ferrous metals. Careful selection of the components in a molecule designed for inhibiting corrosion permits a tightly-packed hydrophobic film to be formed, which prevents corrosive materials from reaching the metal surface.

Detergents and Dispersants

The terms "detergent" and "dispersant" are often used interchangeably when discussing engine oils. If a distinction is made, detergents are normally considered for deposit control at high temperatures and dispersants for controlling low-temperature sludge.

Detergents — When engines operate at high temperatures, the engine oil is an important heat-transfer fluid that prevents overheating of areas such as piston rings, undercrowns, and skirts. Exposure to these localized high temperatures and blowby gas accelerates the rate of oil decomposition to produce deposits[19]. These deposits can prevent free movement of piston rings and keep them from forming the desired seal between the piston and cylinder wall. Varnish or lacquer deposits that can form on the piston undercrown and skirts reduce the rate at which the piston can transfer heat to the engine oil.

The products of high-temperature lubricant oxidation are highly-acidic polar oxygenates which have low solubility in mineral oil and a strong affinity for other polar compounds and metal surfaces. They readily polymerize, and when trapped in ring grooves they further decompose to hard carbonaceous deposits[19,24]. Detergency as measured in the ASTM Sequence VC Test is illustrated in Figure 19.

Typical detergent additives are normal or basic barium, calcium, or magnesium salts of substituted long-chain alkyl compounds. They react with the highly-acidic deposit precursors to neutralize them and keep them in suspension as very small particles.

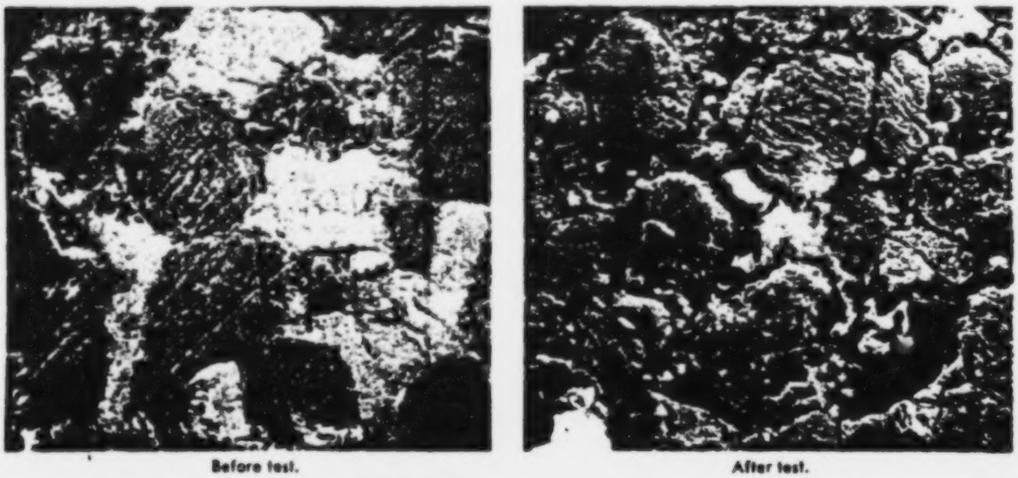
Dispersants — Engines operated under light-duty, short-trip, stop-and-go conditions rarely reach normal operating temperatures. This type of service leads to formation of sludge which coats interior engine parts and can block oil passages. Sludge is a complex mixture of products from fuel combustion, water, carbon, and oxidized oil that has agglomerated and is no longer soluble in the engine oil. Typical dispersants have a polar functional group appended to a large hydrocarbon group. This enables them to adsorb on contaminant particles such as soot or lead halides and keep them in suspension so that they cannot agglomerate to form sludge[19,24].

Figure 20 illustrates dispersancy as measured in taxi testing. In contrast to detergents, which are often metal salts of organic acids, dispersants usually do not contain metallic components and are therefore called "ashless". These additives are prepared by incorporating polar functionality from amines, amides, phosphorus esters or anhydrides with methacrylate or olefin polymers. Substituted long-chain alkenyl succinimides are one of the many classes of additives that have gained acceptance as ashless dispersants.

Automatic transmission fluids are not required to contend with the quantities of contamination typical of engine oils, but they still must prevent sludge formation. Wear debris from clutch plates and oil decomposition products are kept from forming sludge by the same types of ashless dispersants used in engine oils[25].

Friction Modifiers

Automatic transmissions, limited-slip differentials, power take-off units and wet-brake systems require lubricants with specific frictional properties for proper clutch engagement. Some units require a quick clutch lock-up, while others require a small amount of slippage prior to lock-up for a smooth engagement. A majority of the frictional require-



Before test. **After test.**

Dark areas are copper . . . light areas are lead.

Figure 18 — Scanning electron micrographs (870X magnification) showing lead corrosion of a copper-lead bearing in an L-38 engine test.

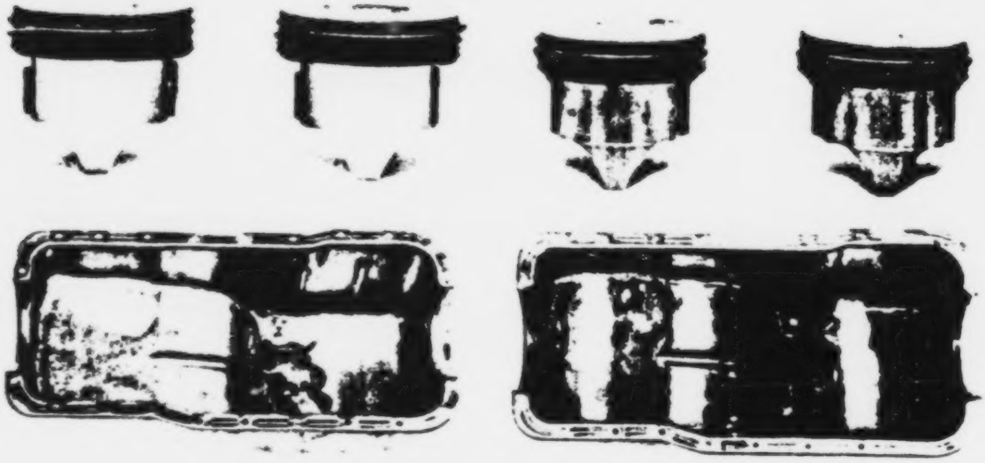


Figure 19 — Detergency as measured in the ASTM Sequence VC Test.

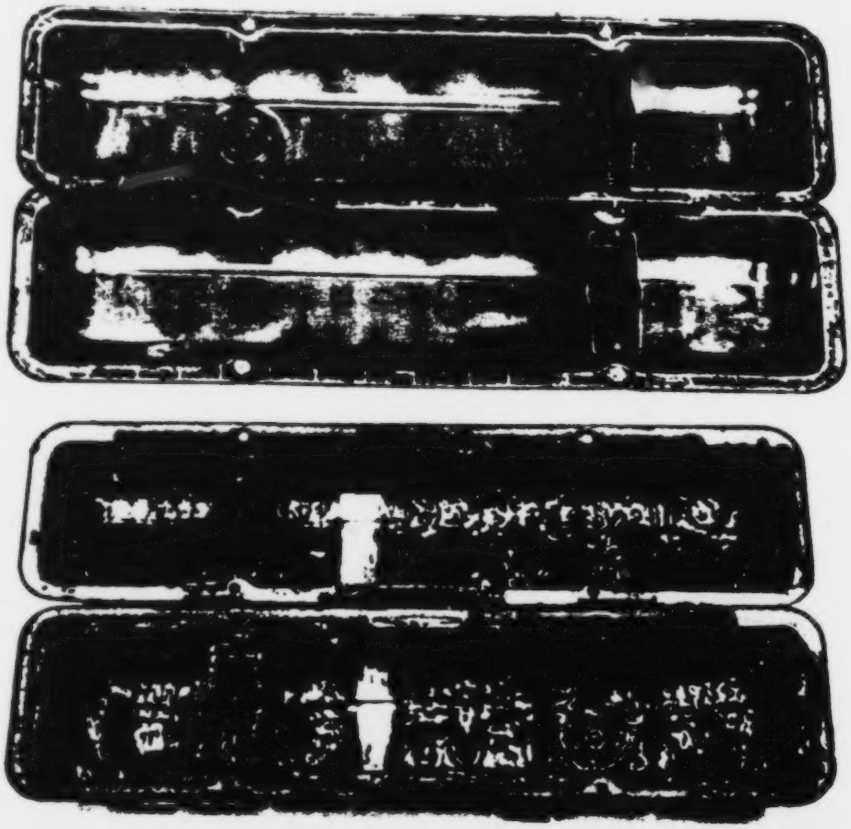


Figure 20 — Dispersancy as measured in taxi testing.

Reproduced from best available copy.

TABLE II
PERFORMANCE ADDITIVES
AUTOMOTIVE LUBRICANTS

Additive Type	Purpose	Typical Compounds	Functions
Pour Point Depressant	Enable lubricant to flow at low temperatures	Alkylated naphthalene and phenolic polymers, polymethacrylates	Modify wax crystal formation to reduce interlocking
Seal Swell Agent	Swell elastomeric seals	Organic phosphates, aromatics, halogenated hydrocarbons	Chemical reaction with elastomer to cause slight swell
Viscosity Index Improver	Reduce the rate of viscosity change with temperature	Polymers and copolymers of methacrylates, butadiene, olefins and alkylated styrenes	Polymers expand with increasing temperature to counteract oil thinning

ments are determined by equipment design and the materials used for clutch plates. The dynamic and static coefficients of friction can also be modified to provide the desired lock-up characteristics by changing the viscosity of the lubricant and the choice of the additives[25,26].

Organic fatty acids have been used to provide a smoother shift in automatic transmissions. Sulfurized fatty acids and fatty amines have been used to reduce the undesirable stick-slip conditions that produce chatter and squawk sometimes associated with clutch lock-up[27]. The additives used as friction modifiers must not cause slippage once lock-up has occurred, since excessive slippage would produce high surface temperatures which could result in glazing of the clutch plates and ultimate frictional failure of the transmission.

Performance Additives

Table II lists examples of these additives.

Pour Point Depressants

Mineral oils thin out at high temperatures and thicken at low temperatures. These are natural properties of the oil that are determined by the crude oil and the refinery processing which it receives. Mineral oils selected for a particular lubricant should allow that lubricant to remain fluid over the entire temperature range it may encounter in service. Paraffin wax present in most refined oils comes out of solution at low temperatures in the form of wax crystals. At these temperatures the oil itself is still capable of flowing, but an interlocking network of wax crystals will not permit flow.

Polymeric additives such as polymethacrylates, or condensation products of chlorinated wax and phenols can be used to interfere with wax crystal growth and alter the formation of the interlocking crystal network.

Seal-Swell Agents

Drive-train designs for transmitting power from engines and gear cases involve the use of elastomeric seals to prevent lubricant leakage and to exclude dirt. Butadiene-acrylonitrile copolymers and silicone elastomers are examples of two of the many compounds commonly used for seals in drive-train components[25]. The seals and the lubricants they come in contact with must be compatible. Significant shrinkage or softening of the seals cannot be tolerated, but a slight swelling is often desirable to improve contact with the moving shafts.

The chemical composition of the base oils themselves can affect seal swell, and this is usually taken into consideration when formulating lubricants. If the base oil does not provide sufficient swell, an aromatic or organic phosphate additive is often used to obtain the desired amount of swelling.

Viscosity Index (VI) Improvers

As mentioned in the section on pour depressants, mineral oils become less viscous as their temperature increases. The rate at which they thin out has been described by a mathematical relationship between their viscosities at 100°F (37.8°C) and 210°F (98.9°C), which is referred to as viscosity index (VI)[28]. Oils with a low VI exhibit a greater viscosity change with temperature than oils with a higher VI. A lubricant that is expected to perform over a wide temperature range must usually have a high VI. The viscosity index of automotive engine oils has received considerable attention because ease of starting requires low viscosity at low temperatures, but normal operation requires maintaining an adequate fluid film near 300°F (149°C).

Mineral oils have been able to meet these wide-temperature-range viscosity requirements through use of high-molecular-weight polymeric additives known as VI improvers. At low temperatures, these polymers are barely soluble in the oil and exist as closely coiled chains with little influence on viscosity of the oil. As the temperature increases, the polymer becomes more soluble and expands into loose, random coils. These expanded polymers restrict movement of the oil molecules and serve to reduce the rate at which oil thins out with increasing temperature. Figure 21 illustrates the effect of a VI improver on viscosity and viscosity index.

TABLE III
LUBRICANT PROTECTIVE ADDITIVES AUTOMOTIVE LUBRICANTS

Additive Type	Purpose	Typical Compounds	Functions
Antifoamant	Prevent lubricant from forming a persistent foam	Silicone polymers, organic copolymers	Reduce surface tension to speed collapse of foam
Antioxidant	Retard oxidative decomposition	Zinc dithiophosphates, hindered phenols, aromatic amines, sulfurized phenols	Decompose peroxides and terminate free-radical reactions
Metal Deactivator	Reduce catalytic effect of metals on oxidation rate	Organic complexes containing nitrogen or sulfur, amines, sulfides and phosphites	Form inactive film on metal surfaces by complexing with metallic ions

Various methacrylates, olefin copolymers, and copolymers of styrene have been used as VI improvers. The amount of thickening they provide depends on the size of the polymer molecule. A larger or higher-molecular-weight polymer of the same type will generally contribute more thickening. Shear stability is another important property of VI improvers. Larger long-chain polymers are more likely to be broken apart by shear forces between moving surfaces. Once this type of permanent shearing takes place, the polymer contributes less high-temperature thickening. Therefore, formulation of high VI oils using polymeric VI improvers requires selection of a polymer that will continue to provide adequate high-temperature thickening in service.

Lubricant Protective Additives

Examples of these additives are listed in Table III.

Antifoamants

All automotive lubricants which are subjected to sufficient agitation will entrain air and produce foam. This is undesirable because it increases exposure of the lubricant to oxygen and thereby increases the rate of oxidative decomposition. Entrained air and foam also reduce lubricant efficiency as a coolant and hydraulic fluid. Polymers of silicone and organic copolymers are commonly used to control foam. These additives have lower surface tension than the lubricant and low solubility in the lubricant. This permits them to spread over the surface of foam bubbles at a concentration high enough to weaken the oil film, causing it to rupture[29].

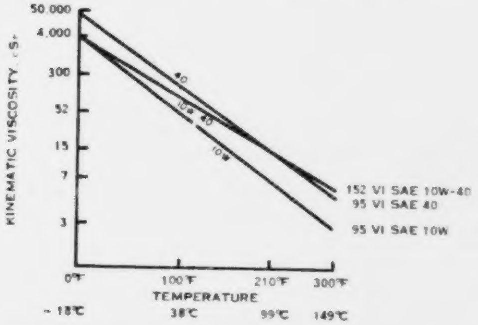


Figure 21 — The effect of a VI improver on viscosity and viscosity index.

Antioxidants

Additives that reduce oil oxidation, and in many cases also reduce corrosion, are called antioxidants. Much has been written about the nature of oxidation, but it is not yet fully understood in all of its aspects. The process is extremely complex[30].

In oxidation, it is generally theorized that organic peroxides are formed by the removal of a hydrogen atom from the hydrocarbon chain with the resultant formation of a "free radical":

$$\text{RH (hydrocarbon)} \rightarrow \text{R}\cdot \text{ (free radical)} + \text{H}\cdot$$

which then reacts with oxygen to form a peroxy radical:

$$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot \text{ (peroxy radical)}^{31}$$

These peroxy radicals act as the precursors for further oxidation. They may remove a hydrogen atom from another hydrocarbon molecule to form a hydroperoxide and another free radical in a chain reaction:

$$\text{ROO}\cdot + \text{RH} \rightarrow \text{ROOH (hydroperoxide)} + \text{R}\cdot$$

The process is further complicated by decomposition reactions:

$$\text{ROOH} \rightarrow \text{RO}\cdot + \text{OH}\cdot$$

which result in a variety of organic compounds such as aldehydes, alcohols, ketones, and acids which may further oxidize and react with each other to form high-molecular-weight polymers. Some of these polymers may be oil soluble, resulting in a viscosity increase of the lubricant; others may be oil insoluble and drop out as varnish or sludge.

Both the initiation and continuation of the oxidation are materially affected by temperature [in

TABLE IV
FUNCTIONS AND TYPES OF AUTOMOTIVE DRIVE-TRAIN LUBRICANT ADDITIVES

Surface Protective Additives	**Performance Additives**	**Lubricant Protective Additives**
Antiwear Agents	Pour Point Depressants	Antifoamants
Corrosion Inhibitors	Seal Swell Agents	Antioxidants
Detergents	Viscosity Index (VI) Improvers	Metal Deactivators
Dispersants		
Extreme Pressure (EP) Agents		
Friction Modifiers		
Rust Inhibitors		

general, oxidation rates are roughly doubled for each 10°C (18°F) rise in temperature], but may also be catalyzed by light or by the presence of various metals. Even minute amounts of some metals may have a marked effect on oxidation.

The termination of the oxidation reaction may result from the exhaustion of the oxygen supply—which is not usual in lubrication systems where there is normally at least some contact with the atmosphere—or from the formation of end products that are too stable to participate further in the oxidation chain reaction:

$$2\,R\cdot \rightarrow RR$$

Oxidation inhibitors, or antioxidants, may function as chain-terminating agents by reacting with free radicals to form stable products, by acting as peroxide decomposers, or they may act as metal passivators to prevent catalytic effects. The chain terminating additives are usually organic aromatic amines, phenols, or sulfides. Those that inhibit the catalytic effect of metallic ions are generally organic sulfides, phosphites, or thiophosphates. Although oxidation and corrosion inhibitors are frequently referred to separately, many of the phosphorus- and sulfur-containing compounds are effective in both applications.

The entire matter of oxidation is affected by many things, including the earlier-mentioned temperature of the lubricant and by the materials of construction of the equipment in which the lubricant is used. It is also materially affected by the inherent resistance of the lubricant itself to oxidation. This resistance is affected by crude source and refining process (which in turn affects the relative amounts of paraffinic, aromatic and naphthenic hydrocarbons). Because of these fundamental differences, lubricants respond differently to different additives. The final choice of the additive must be based, therefore, on actual tests in the lubricant to be inhibited.

Metal Deactivators

In the discussion of oxidation inhibitors, metals such as copper, iron, and lead were said to catalyze oxidation. Additives that can form a coating on metallic catalysts to prevent them from entering into reactions are variously referred to as metal deactivators, metal passivators, or catalyst poisons. Materials previously covered as corrosion and rust inhibitors also function as metal deactivators, due to their ability to form a coating on the metal surface.

Table IV summarizes and condenses the information on the various groups and types of additives used in automotive drive-train lubricants.

INDUSTRIAL LUBRICANT ADDITIVES

This section examines some of the more common additives used in industrial oils and greases. These include oiliness, film strength, EP (extreme pressure), and antiwear agents; corrosion inhibitors and rust inhibitors; pour depressants and viscosity index improvers; emulsifiers and demulsifiers; tackiness agents; oxidation inhibitors; antifoamants; bactericides, bacteriostats, and fungicides; and miscellaneous additives. These additives, either singly or in various combinations, are used in a variety of industrial lubricants. A few examples include metal working lubricants, industrial greases, industrial gear lubricants, transformer oils, hydraulic oils, refrigeration oils, turbine oils, compressor oils, rock drill lubricants, paper machine oils, way lubricants, and railway journal box oils.

Similar to automotive lubricant additives, industrial lubricant additives can be classified into three main functional types: those which (1) protect the lubricated surface, (2) improve lubricant performance, and (3) protect the lubricant.

Surface Protective Additives

Examples of these additives are listed in Table V.

Oiliness, Film Strength, EP and Antiwear Agents

For many years, the film strength of straight mineral oils was adequate for many purposes. With longer drain intervals and increased power output and capacity for equipment of a given size, however, the unit loading and resultant pressures on critical parts increased. These higher loads led to the development of so-called oiliness, film strength, extreme pressure and antiwear agents. The basic purpose for

TABLE V

SURFACE PROTECTIVE ADDITIVES INDUSTRIAL LUBRICANTS

Additive Type	Purpose	Typical Compounds	Functions
Oiliness Agent	Reduce friction under near-boundary conditions	High-molecular-weight compounds such as fatty oils, oxidized waxes or lead soaps	Adherence of polar materials to metal surfaces
Extreme Pressure (EP) Agent	Prevent galling, scoring and seizure	Sulfur-, chlorine-, and phosphorus-containing materials, sometimes with lead soaps	Formation of low shear films on metal surfaces at point of contact
Antiwear Agent	Reduce wear	Organic phosphates and phosphites, zinc dithiophosphates	Exert a smoothing action to form ultra-fine finishes
Corrosion Inhibitor	Prevent corrosive attack on alloy bearings or on other metallic surfaces	Organic compounds containing active sulfur, phosphorus or nitrogen, such as phosphites, metal salts of thiophosphoric acid, sulfurized waxes and terpenes	Inhibits formation of acidic bodies or forms a protective film over the metallic parts
Rust Inhibitor	Prevent or reduce rusting	Sulfonates, amines, fatty oils, oxidized wax, and halogenated derivatives of some fatty acids	Preferential adsorption of polar, surface-active materials, neutralize corrosive acids

the chemical compounds referred to by these general classes is very similar. These materials are used to (1) reduce friction, (2) prevent galling, scoring and seizure, and (3) reduce or minimize wear[31].

As long as the lubrication of a given piece of equipment remains in the so-called hydrodynamic region, the fluid film provided by oil alone is adequate. Once boundary lubrication is reached, however,—that is, when the fluid film becomes very thin —additives are required. Various terms such as oiliness agents, lubricity improvers, film strength enhancers, etc. have been used. The exact mechanism of their functioning in each case is not fully understood, due in part to difficulties of evaluation.

The term "oiliness" is used to indicate differences in friction when different lubricants are used under the same conditions. "Film strength" concerns the loads that can be supported by a film. "EP" (extreme pressure) agents are probably misnamed since the formation of surface compounds of relatively low shear strength is brought about by high temperatures (which are experienced under extremely high pressure conditions) rather than by high pressures as such. "Antiwear" agents apparently function through a chemical polishing action on the bearing surfaces.

Fatty acid esters and fatty alcohols are among the commonly used oiliness agents. The EP agents are generally compounds containing chlorine, sulfur, and/or phosphorus. In the case of gear oils and greases, the primary EP agents have been combinations of sulfur-containing materials and lead soaps. More recently, the heavy metals have become suspect in many applications for toxicological reasons, so the non-lead additives are now in wide use. Zinc, phosphorus, and sulfur compounds such as tricresylphosphate and zinc dithiophosphate have been found to be effective as antiwear agents. Also, sulfur-phosphorus systems containing no metals may be effective.

The effectiveness of an additive depends on the base fluid, other additives, and the operating conditions. The best additive for one system may not be effective in another. Also, multi-additive packages must be balanced for a given product[32].

Corrosion Inhibitors

These materials are added to lubricants to protect against chemical attack of alloy bearings and metal surfaces. As previously indicated, oxidation inhibitors are also corrosion inhibitors to a degree since they prevent—or at least delay—the formation of oxidation products which may be chemically active insofar as the metals present are concerned. Other components, naturally present or added to various lubricants, may also be chemically active. The use of corrosion inhibitors is therefore common.

Corrosion inhibitors function by reacting chemically with the nonferrous metal components, e.g. copper-lead or lead-bronze bearings, to form a corrosion-resistant, protective film[33].

The major classes of corrosion inhibitors in commercial use at the present time include: (1) metal diorganodithiophosphates, (2) metal diorganodithiocarbamates, (3) sulfurized terpenes, (4) phosphosulfurized terpenes, and (5) heterocyclics such as benzotriazole.

Rust Inhibitors

Although rusting is a form of oxidation, it is being considered separately because rust inhibition is concerned primarily with the protection of the equipment itself rather than preventing oxidation of the lubricant.

TABLE VI
PERFORMANCE ADDITIVES INDUSTRIAL LUBRICANTS

Additive Type	Purpose	Typical Compounds	Functions
Pour Point Depressant	Lower the pour point of lubricating oils	Alkylated naphthylene or phenols and their polymers, methacrylate polymers	Modification of wax crystals to prevent growth with accompanying solidification at low temperatures
Viscosity Index (VI) Improver	Lower the rate of change of viscosity with temperature	Polymerized olefins or iso-olefins, butylene polymers, alkylated styrene polymers, polymethacrylate	Because of differences in solubility, viscosity at high temperature is raised more than viscosity at low temperature
Emulsifier	To give emulsions of the water-in-oil or oil-in-water type, depending on application	Soaps of fatty acids, sulfonic acids or naphthenic acids	Surface-active agents change interfacial tension
Demulsifier	Loosen and break stable emulsions	Heavy metal soaps, alkaline earth sulfonates	Lower emulsion stability
Tackiness Agent	Increase adhesiveness of lubricant on metal surfaces	High molecular weight polymers, aluminum soaps of unsaturated fatty acids	Increases viscosity of lubricant and imparts adhesive characteristics

Moisture due to machine operating conditions, for example in circulating systems of steam turbines, steel mills, paper machines, etc., may be present either as free water or as entrainment in the lubricant. Rust inhibitors prevent water from penetrating the protective oil film. This is accomplished by improving the ability of the oil to adhere tenaciously to the metallic machine surfaces (ball and roller bearings, steel shafting, gear teeth, etc.) or, if the amount of moisture is small and operations permit, by emulsifying the moisture so that it does not contact the metal surfaces.

Typical of the materials used for rust inhibition are alkenylsuccinic acids and their derivatives, alkylthioacetic acid derivatives, substituted imidazolines, amine phosphates, and metal and amine sulfonates. In the case of lubricating greases, if only small amounts of water are present, sodium soap greases have generally very good rust inhibition because of their ability to absorb and emulsify the water. If large quantities of water are involved, as for example in steel mill operations, sodium soap greases are not satisfactory because of high water washout losses. In these cases, water-repellent greases are used, sometimes with additives to improve water repellency. Certain organic silicone polymers and some aliphatic amines are useful in this type of application.

Performance Additives

Examples of these additives are listed in Table VI.

Pour Depressants and Viscosity Index (VI) Improvers

Industrial lubricants are at times used under low temperature conditions. The same general types of additives are used as for automotive oils, i.e., various polymers to modify wax crystal growth or to change the viscosity-temperature profile of the lubricant.

Emulsifiers

In most lubrication applications, emulsification is an undesirable characteristic. In some specific types of usage, however, lubricants are purposely compounded with emulsifying agents. In the case of the fire-resistant hydraulic fluids, water-in-oil emulsions are desired. In this case the primary function of the fluid is still lubrication—the water incorporated in the fluid serves primarily to decrease the flammability of the oil. These products are, therefore, safer for use in mines and other locations where low flammability is needed for safety reasons.

In the metal working area—cutting and grinding of metals—the primary need is for cooling. In this case, oil-in-water emulsions are desired. The oil, with added emulsifiers, is normally sold as such and the product is emulsified with water at the point of use.

A wide variety of emulsifiers have been used. For water-in-oil emulsions, typical emulsifiers include ethylene oxide condensation products, some metal sulfonates, derivatives of polyhydroxy alcohols such as sorbitol, and sulfosuccinates. For oil-in-water emulsions, i.e., "soluble oils," surface-active agents which reduce the interfacial tension sufficiently so that the oil can be finely dispersed in water are used. Soaps of fatty acids, sulfonic acids, rosins, or naphthenic acids have been used for this purpose. In any case, a delicate balance between emulsifier ratios and alkalinity must be achieved; this must be established for each system and cannot be broadly predicted.

TABLE VII

LUBRICANT PROTECTIVE ADDITIVES INDUSTRIAL LUBRICANTS

Additive Type	Purpose	Typical Compounds	Functions
Antioxidant	Prevent varnish and sludge, prevent corrosion of alloy bearings	Organic compounds containing sulfur, phosphorus or nitrogen, i.e., organic sulfides, amines or hydroxy sulfides	Terminates oil oxidation reactions by the formation of inactive compounds or by taking up oxygen
Antifoamant	Prevent formation of stable foam	Silicone polymers, organic polymers	Change interfacial tension to permit coalescence of small bubbles; large bubbles separate faster
Bactericide, Bacteriostat and Fungicide	Control of bacteria and fungi to control odor, emulsion breaking and metal staining	Certain alcohols, aldehydes, phenols and chlorine-containing compounds	Prevention of growth of bacteria and fungi

Demulsifiers

In those cases where emulsification with water is undesirable, demulsifiers may be used. Frequently, these are heavy metal soaps or alkaline earth sulfonates which are antagonistic to emulsion formation in the system involved.

Tackiness Agents

In some cases it is highly desirable that lubricants cling very closely to the lubricated parts and not run off. Good examples would be in the lubrication of textile machinery where runoff would be deleterious to the product, or in the case of track roll lubrication where bearings tend to be loose fitting. High-molecular-weight polymers and some aluminum soaps of high-molecular-weight fatty acids have been used successfully as additives in such applications.

Lubricant Protective Additives

Table VII lists a number of these additives.

Oxidation Inhibitors (Greases)

The oxidation inhibition of greases presents several problems not normally found with industrial lubricating oils. Greases are thickened oils; the thickeners most commonly used are metallic soaps of fatty materials. The presence of the fatty material, particularly where there is some degree of unsaturation (i.e., where double bonds are present in the molecule), makes highly vulnerable sites available for the initiation of the oxidation reaction. Aromatic amines serve well as oxidation inhibitors for greases.

Antifoamants

One of the problems that has been experienced for many years with lubricating oils is excessive foam. There are many situations where petroleum lubricants are used in which entrainment of air or other gases is inevitable. Unless these gases can be released, a foam results. Foams may displace oil from the system, causing improper functioning of pumps, reduced oil flow, enhanced oxidation of the lubricant, and other difficulties.

Silicone polymers have been used very successfully for the release of foam in many situations. In some cases, however, these materials may result in higher air entrainment in the liquid. In these cases, other antifoamants, such as some of the polyacrylates and other organic polymers may be more effective.

Bactericides, Bacteriostats and Fungicides

The problem of bacterial control is closely allied to the problem of emulsion stability. Bacteria in large systems containing soluble oil type oil-in-water emulsions are at times a problem. This is particularly true in cases where weekend shutdowns are involved. Bacterial growth results in bad odors and emulsion degradation. The common bacteria are pseudomonas oleovorans and similar types; the emulsions are normally not af-

TABLE VIII

MISCELLANEOUS ADDITIVES INDUSTRIAL LUBRICANTS

Additive Type	Purpose	Typical Compounds	Functions
Dye	Provide distinctive or attractive color	Oil-soluble compounds with high coloring power	Highly colored materials dissolve to impart color
Odorant	Provide distinctive or pleasant odors or mask undesirable odors	Oil-soluble synthetic perfumes	Small amounts of highly fragrant substances impart odor to lubricants

TABLE IX
FUNCTION AND TYPES OF INDUSTRIAL LUBRICANT ADDITIVES

Surface Protective Additives	Performance Additives	Lubricant Protective Additives	Miscellaneous Additives
Oiliness Agents	Pour Point Depressants	Antioxidants	Dyes
Extreme Pressure (EP) Agents	Viscosity Index (VI) Improvers	Antifoamants	Odorants
Antiwear Agents	Emulsifiers	Bactericides, Bacteriostats and Fungicides	
Corrosion Inhibitors	Demulsifiers		
Rust Inhibitors	Tackiness Agents		

fected by pathogenic varieties. To control bacteria and fungi, antiseptics and bactericides containing certain alcohols, phenols, and chlorine-containing materials have been used.

Miscellaneous Additives

A complete discussion of all the areas where enhancement of lubricant properties or the achievement of desired qualities have been brought about by the use of additive materials is beyond the scope of this article. A few of the other areas include the use of dyes to obtain a desired or distinctive color or a uniformity of color, and odorants to provide a distinctive odor or to mask undesirable odors. Examples of these are listed in Table VIII.

Table IX summarizes and condenses the information on the various groups and types of additives used in industrial lubricants.

One additional item should at least be given mention. It should be evident from the foregoing that choosing additives for a lubricant to accomplish a specific purpose is not something that can be done in a haphazard way. Many times additives may have interacting effects so that undesirable side reactions may be experienced if additives are mixed without full consideration of these reactions. Since it is frequently necessary to use a number of different additives, the total additive "package" must be carefully balanced. The user of quality lubricants can rest assured that much care and testing has gone into the correct balancing of the total package.

SUMMARY

The petroleum industry makes extensive use of additives throughout its operation. This article has presented in condensed form, the rationale for using additives in fuels, automotive drive-train lubricants, and industrial lubricants. Enormous amounts of time, scientific talent and money are spent formulating and evaluating additives for use in these products. All this is done to insure that a customer will be able to obtain a petroleum product that satisfies his performance requirements.

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FUEL AND LUBRICATING OILS FOR DETROIT DIESEL ENGINES

This bulletin presents guidelines for the fuels and lubricants best suited for good performance and long life in Detroit Diesel engines.

DIESEL FUEL OILS GENERAL CONSIDERATIONS

The quality of fuel oil used for high-speed diesel engine operation is a very important factor in obtaining satisfactory engine performance, long engine life, and acceptable exhaust.

Fuel selected should be completely distilled material. That is, the fuel should show at least 98% by volume recovery when subjected to ASTM D-86 distillation. Fuels marketed to meet Federal Specification VV-F-800 (grades DF-1 and DF-2) and ASTM Designation D-975 (grades 1-D and 2-D) meet the completely distilled criteria. Some of the general properties of VV-F-800 and ASTM D-975 fuels are shown below.

FEDERAL SPECIFICATION & ASTM DIESEL FUEL PROPERTIES

Specification or Classification Grade	VV-F-800 DF-1	ASTM D-975 1-D	VV-F-800 DF-2	ASTM D-975 2-D
Flash Point, min.	104° F 40° C	100° F 38° C	122° F 50° C	125° F 52°C
Carbon Residue (10% residuum), % max.	0.15	0.15	0.20	0.35
Water & Sediment, % by vol., max.	0.01	trace	0.01	0.05
Ash, % by wt., max.	0.005	0.01	0.005	0.01
Distillation Temperature, 90% by vol. recovery, min.	—	—	—	540°F (282°C)
max.	572°F (300°C)	550°F (288°C)	626°F (330°C)	640°F (338°C)
End Point, max.	626°F (330°C)	—	671°F (355°C)	—
Viscosity 100°F (38°C)				
Kinematic, cs, min.	1.4	1.4	2.0	2.0
Saybolt, SUS, min.	—	—	—	32.6
Kinematic, cs, max.	3.0	2.5	4.3	4.3
Saybolt, SUS, max.	—	34.4	—	40.1
Sulfur, % by wt., max.	0.50	0.50	0.50	0.50
Cetane No.	45	40	45	40

Residual fuels and domestic furnace oils are not considered satisfactory for Detroit Diesel engines; however, some may be acceptable. (See "DETROIT DIESEL FUEL OIL SPECIFICATIONS.")

NOTE: Detroit Diesel Allison does not recommend the use of drained lubricating oil as a diesel fuel oil. Furthermore, Detroit Diesel Allison will not be responsible for any engine detrimental effects which it determines resulted from this practice.

All diesel fuel oil contains a certain amount of sulfur. Too high a sulfur content results in excessive cylinder wear due to acid build-up in the lubricating oil. For most satisfactory engine life, fuels containing less than 0.5% sulfur should be used.

Fuel oil should be clean and free of contamination. Storage tanks should be inspected regularly for dirt, water or water-emulsion sludge, and cleaned if contaminated. Storage instability of the fuel can lead to the formation of varnish or sludge in the tank. The presence of these contaminants from storage instability must be resolved with the fuel supplier.

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DETROIT DIESEL FUEL OIL SPECIFICATIONS

Detroit Diesel Allison designs, develops, and manufactures commercial diesel engines to operate on diesel fuels classified by the ASTM as Designation D-975 (grades 1-D and 2-D). These grades are very similar to grades DF-1 and DF-2 of Federal Specification VV-F-800. Residual fuels and furnace oils, generally, are not considered satisfactory for Detroit Diesel engines. In some regions, however, fuel suppliers may distribute one fuel that is marketed as either diesel fuel (ASTM D-975) or domestic heating fuel (ASTM D-396) sometimes identified as furnace oil. In this case, the fuel should be investigated to determine whether the properties conform with those shown in the "FUEL OIL SELECTION CHART" presented in this specification.

The "FUEL OIL SELECTION CHART" also will serve as a guide in the selection of the proper fuel for various applications. The fuels used must be clean, completely distilled, stable, and non-corrosive. DISTILLATION RANGE, CETANE NUMBER, and SULFUR CONTENT are three of the most important properties of diesel fuels that must be controlled to insure optimum combustion and minimum wear. Engine speed, load, and ambient temperature influence the selection of fuels with respect to distillation range and cetane number. The sulfur content of the fuel must be as low as possible to avoid excessive deposit formation, premature wear, and to minimize the sulfur dioxide exhausted into the atmosphere.

To assure that the fuel you use meets the required properties, enlist the aid of a reputable fuel oil supplier. The responsibility for clean fuel lies with the fuel supplier as well as the operator.

During cold weather engine operation, the cloud point (the temperature at which wax crystals begin to form in diesel fuel) should be 10°F (6°C) below the lowest expected fuel temperature to prevent clogging of the fuel filters by wax crystals.

At temperatures below −20°F (−29°C), consult an authorized Detroit Diesel Allison service outlet, since particular attention must be given to the cooling system, lubricating system, fuel system, electrical system, and cold weather starting aids for efficient engine starting and operation.

FUEL OIL SELECTION CHART

Typical Application	General Fuel Classification	Final Boiling Point	Cetane No.	Sulfur Content
		(Max.)	(Min.)	(Max.)
City Buses	No. 1-D	550°F (288°C)	45	0.30%
All Other Applications	Winter No. 2-D Summer No. 2-D	675°F 675°F (357°C)	45 40	0.50% 0.50%

NOTE: When prolonged idling periods or cold weather conditions below 32°F (0°C) are encountered, the use of lighter distillate fuels may be more practical. The same consideration must be made when operating at altitudes above 5,000 ft.

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DIESEL LUBRICATING OILS GENERAL CONSIDERATIONS

All diesel engines require heavy-duty lubricating oils. Basic requirements of such oils are lubricating quality, high heat resistance, and control of contaminants.

LUBRICATING QUALITY. The reduction of friction and wear by maintaining an oil film between moving parts is the primary requisite of a lubricant. Film thickness and its ability to prevent metal-to-metal contact of moving parts is related to oil viscosity. The optimums for Detroit Diesel engines are 15W-40, or SAE 40 or 30 weight.

HIGH HEAT RESISTANCE. Temperature is the most important factor in determining the rate at which deterioration or oxidation of the lubricating oil will occur. The oil should have adequate thermal stability at elevated temperatures, thereby precluding formation of harmful carbonaceous and/or ash deposits.

CONTROL OF CONTAMINANTS. The piston and compression rings must ride on a film of oil to minimize wear and prevent cylinder seizure. At normal rates of consumption, oil reaches a temperature zone at the upper part of the piston where rapid oxidation and carbonization can occur. In addition, as oil circulates through the engine, it is continuously contaminated by soot, acids, and water originating from combustion. Until they are exhausted, detergent and dispersant additives aid in keeping sludge and varnish from depositing on engine parts. But such additives in excessive quantities can result in detrimental ash deposits. If abnormal amounts of insoluble deposits form, particularly on the piston in the compression ring area, early engine failure may result.

Oil that is carried up the cylinder liner wall is normally consumed during engine operation. The oil and additives leave carbonaceous and/or ash deposits when subjected to the elevated temperatures of the combustion chamber. The amount of deposits is influenced by the oil composition, additive content, engine temperature, and oil consumption rate.

DETROIT DIESEL LUBRICATING OIL SPECIFICATIONS

OIL QUALITY

OIL QUALITY is the responsibility of the oil supplier. (The term *oil supplier* is applicable to refiners, blenders, and rebranders of petroleum products, and does not include distributors of such products.)

There are hundreds of commercial crankcase oils marketed today. Obviously, engine manufacturers or users cannot completely evaluate the numerous commercial oils. The selection of a suitable lubricant in consultation with a reliable oil supplier, observance of his oil drain recommendations (based on used oil sample analysis and experience) and proper filter maintenance, will provide the best assurance of satisfactory oil performance.

Detroit Diesel Allison lubricant recommendations are based on general experience with current lubricants of various types and give consideration to the commercial lubricants presently available.

RECOMMENDATION

Detroit Diesel engines have given optimum performance and experienced the longest service life with the following oil performance levels having the ash limits and zinc requirements shown.

15W-40 MULTIGRADE LUBE OIL

Detroit Diesel Allison now approves and recommends the use of the new generation 15W-40 lubricating oils, providing the following ash limits, zinc requirements, oil performance levels, and conditions are met:

1. The sulfated ash (ASTM D-874) content of the lubricant shall not exceed 1.000% by weight, except lubricants that contain only barium detergent-dispersant salts where 1.5% by weight is allowed.
2. The lubricant shall meet the performance requirements shown in API Service Classifications CD/SE.
3. The zinc content (zinc diorganodithiophosphate) of all the lubricants recommended for use in Detroit Diesel engines shall be a minimum of 0.07% by weight. However, the zinc requirement is waived where EMD lubricants are used.
4. Evidence of satisfactory performance in Detroit Diesel engines has been shown to the customer and to Detroit Diesel Allison by the oil supplier.

10W-30, 20W-40 & OTHER MULTIGRADE OILS

Detroit Diesel Allison does *NOT* approve any multigrade oils, except the new generation 15W-40 lubricants previously described. Although lubricants such as 10W-30 and 20W-40 are commercially available, the performance of their additive systems has not been demonstrated in Detroit Diesel engines. Since properties such as sulfated ash are affected in formulating these multigrade compounds, their use cannot be approved.

SAE-40 & SAE-30 SINGLE GRADE LUBRICANTS

Detroit Diesel Allison continues to approve SAE-40 and SAE-30 lube oils, providing they meet the 1.000% maximum sulfated ash limit, the 0.07% by weight minimum zinc content, and the following API Service Classifications:

API Letter Code Service Classification	Military Specification	SAE Grade
CB	MIL-L-2104A (Supplement 1)	40 or 30
CC	MIL-L-2104B	40 or 30
CD/SC	MIL-L-2104C	40 or 30
CD	MIL-L-45199B (Series 3)	40 or 30
CC/SE	MIL-L-46152	40 or 30
Numerous	Universal	40 or 30

MIL-L-46167 ARCTIC LUBE OILS FOR NORTH SLOPE & OTHER EXTREME SUB-ZERO OPERATIONS

Lubricants meeting this specification are used in Alaska and other extreme sub-zero locations. Generally, they may be described as 5W-20 multigrade lubricants made up of synthetic base stock and manifesting low volatility characteristics. Although they have been used successfully in some severe cold regions. Detroit Diesel Allison does not consider their use as desirable as the use of 15W-40 (new generation), SAE-40, or SAE-30 oils with auxiliary heating aids. For this reason, they should be considered only where engine cranking is a severe problem and auxiliary heating aids are not available on the engine.

EMD (RR) OILS

Lubricants qualified for use in Electro-Motive Division (EMD) diesel engines may be used in Detroit Diesel engines provided the sulfated ash (ASTM D-874) content does not exceed 1.000% by weight. These lubricants are frequently desired for use in applications where both Detroit Diesel and Electro-Motive powered units are operated. These fluids may be described as SAE-40 lubricants that possess medium Viscosity Index properties and do not contain any zinc additives.

SYNTHETIC OILS

Synthetic lubricants may be used in Detroit Diesel engines provided the ash limit, zinc requirements, and specified oil performance levels (for example, CD/SE or MIL-L-2104B, etc.) shown elsewhere in this specification are met. Viscosity grades 15W-40 or SAE-40 or SAE-30 are recommended.

EVIDENCE OF SATISFACTORY PERFORMANCE

Detroit Diesel Allison has referred to evidence of satisfactory performance in its lubricant specifications. Detroit Diesel Allison uses controlled field test oil evaluation programs to determine the performance of lubricants. The following briefly describes one method Detroit Diesel Allison uses to evaluate lubricating oil performance. This method may be used as a guideline for oil suppliers with candidate lubricants for Detroit Diesel engines.

1. Select five (5) highway truck (72,000 lbs. GCW) units in the same fleet powered by Detroit Diesel engines. Operate these on the candidate 15W-40 motor oil for 200,000 miles.
2. Select five (5) "sister" highway trucks in the same fleet to operate on a reference SAE-30 or SAE-40 grade lubricant having a history of good performance in Detroit Diesel engines.
3. *Operate the ten (10) oil test engines for 200,000 miles each.* Monitor the oil and fuel consumption during the test period. Record any serious mechanical problems experienced. Disassemble all ten (10) engines at the conclusion of the 200,000 mile period and compare the following:
    - Ring sticking tendencies and/or ring conditions.
    - Piston skirt and cylinder liner scuffing.
    - Exhaust valve face and stem deposits.
    - Overall wear levels.
4. The results obtained from a new candidate 15W-40 lubricant should be comparable to or better than those obtained from SAE 30 or 40 oils.

ENGINE OIL CLASSIFICATION SYSTEM

The American Petroleum Institute (API), the Society of Automotive Engineers (SAE), and the American Society for Testing and Materials (ASTM) jointly have developed the present commercial system for designating and identifying motor oil classifications. The table below shows a cross-reference of current commercial and military lube oil identification and specification systems.

CROSS REFERENCE OF LUBE OIL CLASSIFICATION SYSTEM

APIC Code Letters	Comparable Military or Commercial Industry Specification
CA	MIL-L-2104A
CB	Supplement 1
CC	MIL-L-2104B (see note below)
CD	MIL-L-45199B (Series B)
‡	MIL-L-46152 (supersedes MIL-L-2104B for Military only.)
■	MIL-L-2104C (supersedes MIL-L-45199B for Military only.)
SA	none
SB	none
SC	Auto passenger car 1964 MS oils — obsolete system
SD	Auto passenger car 1968 MS oils — obsolete system
SE	Auto passenger car 1972 MS oils — obsolete system

‡ Oil performance meets or exceeds that of CC and SE oils.

■ Oil performance meets or exceeds that of CD and SC oils.

NOTE: MIL-L-2104B lubricants are obsolete for Military service applications only.

MIL-L-2104B lubricants are currently marketed and readily available for commercial use.

Consult the following publications for complete descriptions:

1. Society of Automotive Engineers (SAE) Technical Report J-183a.
2. Federal Test Method Standard 791a.

OIL CHANGES

Oil change intervals are dependent upon the various operating conditions of the engines and the sulfur content of the diesel fuel used. Oil drain intervals in all service applications may be increased or decreased with experience using a specific lubricant, while also considering the recommendations of the oil supplier. Generally, the sulfur content of diesel fuels supplied throughout the U.S.A. and Canada are low (i.e., less than 0.5% by weight — ASTM D-129 or D-1552 or D-2622). Fuels distributed in some overseas locations may contain higher concentrations of sulfur, the use of which will require reduced lube oil drain intervals.

Highway Trucks & Inter-City Buses
(Series 71 and 92 Naturally Aspirated and Turbocharged Engines)

For highway trucks and buses used for inter-city operation, the oil change interval is 100,000 miles. The drain interval may be extended beyond this point if supported by the results obtained from used lube oil analysis; it is recommended that you consult with your lube oil supplier in establishing any drain interval exceeding 100,000 miles.

City Transit Coaches and Pick-Up and Delivery Truck Service (Series 53, 71 and 92 Naturally Aspirated and Turbocharged Engines)

For city transit coaches and pick-up and delivery truck service, the oil change interval is 12,500 miles. The oil drain interval may be extended beyond 12,500 miles if supported by used oil analyses.

Industrial and Marine
(Series 53, 71, and 92 Naturally Aspirated and Turbocharged Engines)

Series 53, 71, and 92 engines, in industrial and marine service, should be started with 150-hour oil change periods. The oil drain intervals may be extended if supported by used oil analyses.

Large Industrial and Marine
(Series 149 Naturally Aspirated and Turbocharged Engines)

The recommended oil change period for naturally aspirated Series 149 engines is 500 hours, while the change period for turbocharged Series 149 engines is 300 hours. These drain intervals may be extended if supported by used oil analyses.

Used Lube Oil Analysis Warning Values

The presence of ethylene glycol in the oil is damaging to the engine. Its presence and need for an oil change and for corrective maintenance action may be confirmed by glycol detector kits which are commercially available.

Fuel dilution of the oil may result from loose fuel connections or from prolonged engine idling. A fuel dilution exceeding 2.5% of volume indicates an immediate need for an oil change and corrective maintenance action. Fuel dilution may be confirmed by ASTM D-322 test procedure performed by oil suppliers or independent laboratories.

In addition to the above considerations, if any of the following occur, the oil should be changed:

1. The viscosity at 100° F. of a used oil sample is 40% greater than the viscosity of the unused oil measured at the same temperature (ASTM D-445 and D-2161).
2. The iron content is greater than 150 parts per million.
3. The coagulated pentane insolubles (total contamination) exceed 1.00% by weight (ASTM D-893).
4. The total base number (TBN) is less than 1.0 (ASTM D-664). Note: The sulfur content of the diesel fuel used will influence the alkalinity of the lube oil. With high sulfur fuels, the oil drain interval will have to be shortened to avoid excessive acidity in the lube oil.

LUBE OIL FILTER ELEMENT CHANGES

Full-Flow Filters

A full-flow oil filtration system is used in all Detroit Diesel engines. To ensure against physical deterioration of the filter element, it should be replaced at a *maximum* of 25,000 miles for on-highway vehicles or at each oil change period, whichever occurs first. For all other applications, the filter should be replaced at a *maximum* of 500 hours or at each oil change period, whichever occurs first.

By-Pass Filters

Auxiliary by-pass lube oil filters are not required on Detroit Diesel engines.

PUBLICATION AVAILABLE SHOWING COMMERCIAL "BRAND" NAME LUBRICANTS

A list of "brand" name lubricants distributed by the majority of worldwide oil suppliers can be purchased from the Engine Manufacturers Association (EMA). The publication is titled. *EMA Lubricating Oils Data Book for Heavy-Duty Automotive and Industrial Engines.* The publication shows the brand names, oil performance levels, viscosity grades, and sulfated ash contents of most "brands" marketed.

ENGINE MANUFACTURERS ASSOCIATION
111 EAST WACKER DRIVE
CHICAGO, ILLINOIS 60601

STATEMENT OF POLICY ON FUEL AND LUBRICANT ADDITIVES

In answer to requests concerning the use of fuel and lubricating oil additives, the following excerpt has been taken from a policy statement of General Motors Corporation:

> *"It has been and continues to be General Motors policy to build motor vehicles that will operate satisfactorily on the commercial fuels and lubricants of good quality regularly provided by the petroleum industry through retail outlets."*

Therefore, Detroit Diesel Allison does not recommend the use of any supplementary fuel or lubricant additives. These include all products marketed as fuel conditioners, smoke suppressants, masking agents, reodorants, tune-up compounds, top oils, break-in oils, graphitizers, and friction-reducing compounds.

NOTE: The manufacturer's warranty applicable to Detroit Diesel engines provides in part that the provisions of such warranty shall not apply to any engine unit which has been subject to misuse, negligence or accident. Accordingly, malfunctions attributable to neglect or failure to follow the manufacturer's fuel or lubricating recommendations may not be within the coverage of the warranty.

SERVICE AND INSPECTION INTERVALS

Generally, operating conditions will vary for each engine application, even with comparable mileage or hours and therefore, maintenance schedules can vary. A good rule of thumb for piston ring, and liner inspections, however, would be at 45,000 miles or 1500 hours for the first such inspection and at 30,000 miles or 1000 hour intervals thereafter.

Detroit Diesel Allison
Division of General Motors Corporation

13400 West Outer Drive Detroit, Michigan 48228
In Canada: Diesel Division, General Motors of Canada Limited, London, Ontario

CATERPILLAR TRACTOR CO.

Peoria, Illinois 61629

June 19, 1979

Mr. Thomas M. Baines
Characterization & Applications Branch
U.S. Environmental Protection Agency
Ann Arbor, MI 48105

Dear Tom:

Oil Samples for Nitrosamines Evaluation

This letter is to confirm that we are interested in participating in the EPA diesel crankcase emission characterization program. We look forward to cooperating with EPA in this matter but first we would like to see the results of the MIT evaluation of Dr. Fine's nitrosamine measuring technique.

As you have discussed with R. D. McDowell, the oil samples we will provide are as indicated by the following table:

Engine	Oil Type	Approximate Sampling Schedule As a Fraction of Change Period			
3208 NA	AMOCO 300 (15W40)	New	1/3	2/3	Drain
3406 DIT	Chevron RPM DELO 400 (30W)	New	1/3	2/3	Drain
3406 DITA	Chevron RPM DELO 300 (30W)	New	1/3	2/3	Drain

As shown by the chart, you will be receiving four samples from each engine for a total of 12 samples. The first two engines are operating in trucks owned by a locally based trucking company. The third engine (3406 DITA) will be operating in the lab on an on-highway truck cycle dynamometer test. Along with the oil samples we will supply as much of the requested information as possible. We shall initiate supplying the oil samples whenever you indicate your contractor can accept the samples.

If you have any questions or comments, please contact R. D. McDowell or me.

Very truly yours,

Emissions Control Manager
Engineering G.O.

JCHafele
Ph: (309) 675-5362
sdc

Lubrication

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1 CHEMICAL AND PHYSICAL PROPERTIES

Du Pont Lube Oil Additives 564 and 565 are viscous, straw-colored liquids, mildly basic and completely miscible in all proportions with neutrals and bright stocks. They are insoluble in water. They are methacrylate polymers of the general structure shown in *Figure 1-1*, in which nitrogen has been incorporated into the molecule. This modification of the methacrylate polymers (good viscosity index improvers and pour point depressants) retains the desirable properties of these polymers and adds that of detergency and dispersancy.* They are 40% active ingredient solutions in a light solvent-extracted Mid-Continent neutral oil.

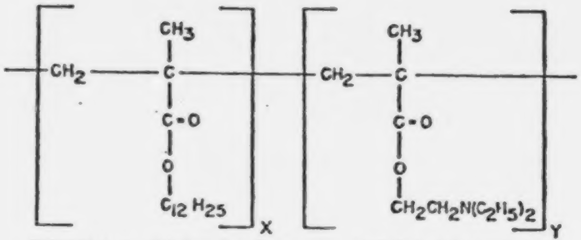

FIGURE 1-1—Molecular Structure of LOA 564 and 565

As shown in *Table 1-1*, this new type of ashless polymeric detergent—VI improver and pour point depressant, is available in two versions, LOA 564 and 565. They differ only in the molecular weight of the active ingredient which affects their relative effectiveness as viscosity index improvers and their shear stability, but does not affect their detergent-dispersant properties.

The change in viscosity of these products with temperature is shown in the section on "Handling."

TABLE 1-1—Typical Physical Properties of LOA 564 and 565

	LOA 564	LOA 565
Viscosity at 210°F, SUS	1200	3800
Viscosity at 100°F, SUS	9000	29,000
Density, lbs./gal.	7.5	7.5
Color, NPA	1—	1—
Pour Point, °F	—10	10
Flash Point (C.O.C.), °F	380	380
Fire Point (C.O.C.), °F	420	420
Total Acid No., mg. KOH/g	0.0	0.0
Total Base No., mg. KOH/g	8.0	8.0
Ash, wt. %	0.00	0.00

**A more detailed description of the chemistry of this class of material and its detergency action may be found in the papers—"A New Class of Polymeric Dispersants for Hydrocarbon Systems" by C. B. Biswell, W. E. Catlin, J. F. Froning and G. B. Robbins (ACS, March 29, 1954, Kansas City, Missouri) and "The Control of Low Temperature Sludge in Passenger Car Engines" by R. L. Willis and E. C. Ballard (SAE, January 11, 1955, Detroit, Michigan).*

Effect on Physical Inspections of Motor Oil

LOA 564 and 565 have little effect on most of the physical inspection tests normally made on motor oils as shown by the physical inspection data presented in *Table 1-2*. Their presence increases the viscosity (thickening), viscosity index, slightly increases the "base number," usually decreases the pour point, and—like all detergents—results in a marked increase in Steam Emulsion number.

TABLE 1-2—Typical Effect on Inspection Tests

Base Oil: Furfural-Extracted Mid-Continent SAE 20 (Oil 27)

ADDITIVES	LOA 564		LOA 565	
Additive, Wt. %	None	3.75	None	3.75
Viscosity at 210°F, SUS	51.5	59.2	51.5	65.7
Viscosity at 100°F, SUS	290	370	296	432
Viscosity Index	94	112	91	120
Gravity, °API at 60°F/60°F	28.3	28.2	28.1	28.1
Density, lbs./gal.	7.37	7.38	7.38	7.38
Color, NPA	6—	6—	6—	6—
Flash Point (C.O.C.), °F	435	425	420	415
Fire Point (C.O.C.), °F	475	465	460	460
Cloud Point, °F	+16	+16	+2	+4
Pour Point, °F	5	—35	5	—35
Carbon Residue (Rams.), Wt. %	0.23	0.20	0.26	0.26
Total Acid No., mg. KOH/g.	0.1	0.0	0.1	0.1
Total Base No., mg. KOH/g.	0.0	0.1	0.0	0.2
Steam Emulsion No.	130	>1200	255	>1200
Ash, Wt. %	0.00	0.00	0.00	0.00
Aniline Point, °C	102.8	102.2	102.2	102.6
Discoloration of Copper Strip				
3 Hrs. at 212°F	None	None	None	None
3 Hrs. at 300°F	None	None	None	None

Shear Stability

Shear stability of oils containing VI improvers takes two forms:

A. *Temporary shear loss.* This is reduced viscosity while the fluid is under mechanical shear. As soon as the fluid is released from the shearing action, it resumes its original viscosity. The magnitude of this effect is dependent upon the rate of shear—the higher the rate of shear the greater the temporary loss.

B. *Permanent loss in viscosity and VI.* This is most probably due to mechanical or oxidative breakdown of the VI improver molecule, which results in a lower average molecular weight of the VI improver with consequent loss of thickening and VI effects.

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Gulf Research & Development Company

D. F. Kendrick
Manager
Petroleum Products Department

P. O. Drawer 2038
Pittsburgh, PA 15230

May 23, 1979
Reference: 5-312LF10

Dr. David Fine
125 Second Avenue
Waltham, Massachusetts 02154

Dear Dr. Fine:

As requested in a telephone conversation with Mr. Tom Bains of EPA, we have shipped to you via UPS 1-quart samples of each of the following Gulf Motor Oils.

Gulf Super Duty Motor Oil 30 - LS-8645
Gulf Super Duty Motor Oil 15W/40 - LS-8646
Gulflube Motor Oil XHD 30 - LS-8647
Gulflube Motor Oil XHD 10W/30 - LS-8648

If you require any information concerning these samples, please contact me at the above address or by phone (412) 665-6241.

Yours very truly,

H. H. Donaldson Jr.

H. H. Donaldson, Jr.

cc: Mr. Tom Bains - Ann Arbor, Michigan

Gulf

A Subsidiary of Gulf Oil Corporation

Telephone 412/665-6000

Mobil Oil Corporation

P.O. BOX 1027
PRINCETON, NEW JERSEY 08540

TECHNICAL SERVICE LABORATORIE

May 3, 1979

J

Dr. David Fine
New England Institute
For Life Sciences
125 2nd Avenue
Waltham, Mass. 02154

SAMPLE SHIPMENTS
MOBIL DELVAC 1230
MOBIL DELVAC SUPER 15W/40

Dear Mr. Fine:

As requested by Mr. T. Baines of the EPA, we shipped to your attention via UPS on May 3, 1979, one quart each of Mobil Delvac 1230 and Mobil Delvac Super 15W/40. It is our understanding that these will be used to determine the contribution of commercial engine oils to the emission of nitrosamines. If there are any questions regarding the samples, please contact these laboratories.

W. A. KENNEDY

NSKotuszenko/dc

cc:
Mr. T. Baines
Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105

Mobil Oil Corporation

150 EAST 42ND STREET
NEW YORK, NEW YORK 10017

June 4, 1979

Mr. Darwin Moon,
Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105

Dear Mr. Moon:

In response to your telephone inquiry about our engine oil, Mobil Delvac 1, the Product Data Sheet and "Facts About Synthetic Lubricants" should give you the information you requested.

The Nitrogen level in new Mobil Delvac 1 is typically about .05%.

I have asked that a quart sample be provided to:

Dr. David Fine,
New England Institute for Life Sciences
125 2nd Avenue
Waltham, Massachusetts 02154

Very truly yours,

G R Jordan

G. R. Jordan
Manager
Marketing Engineering
Division
P. E. S. Department

GRJ:st

Attachments (2)

Delvac 1

Delvac 1

Synthetic Fleet Engine Oil

With the increasing emphasis on fuel conservation, Mobil is continuing to contribute to this effort with the introduction of a synthetic engine oil branded Mobil Delvac 1. It has been developed for use in all types of automotive fleet equipment, including both on-highway and off-highway equipment having either heavy-duty diesel or gasoline engines.

Delvac 1 synthetic engine oil can help because it provides lower fuel consumption (due to reduced friction), lower lube oil consumption, extended oil drain intervals, and longer filter life. The oil is designed to improve cleanliness and reduce wear to ensure longer engine life.

The product has outstanding high-temperature stability, thus ensuring outstanding lubrication under severe engine loads and at critical ambient temperature applications. Concurrently, it also provides exceptional low-temperature fluidity at subzero temperatures that permits faster cranking and easier starting. Delvac 1 is an SAE 30 viscosity oil with low-temperature fluidity comparable to an SAE 5W, to permit proper operation of automotive equipment in extremely cold weather. Delvac 1 utilizes an optimized combination of Mobil-manufactured synthetic base stocks to provide this outstanding wide range of performance characteristics.

Delvac 1 synthetic engine oil meets the performance requirements of U.S. military specifications MIL-L-2104C and MIL-L-46152. It also substantially satisfies the requirements of MIL-L-46167 specifications for subzero engine oil lubrication.

The product exceeds by several-fold key requirements of API CD/SE and Mack Diesel EO-J classifications. Accordingly, Delvac 1 has long-term quality retention in terms of oxidation stability, alkalinity, high-temperature detergency, dispersancy, protection against corrosion, and sludge protection, which can permit extended oil drains and longer filter change intervals.

PRODUCT DESCRIPTION

Delvac 1 synthetic engine oil is a blend of Mobil-produced synthesized hydrocarbons and carefully-selected esters. The lubricant contains a carefully-balanced and custom-designed additive system which provides outstanding high-temperature detergency and unsurpassed dispersancy at both low and high temperatures. The product is highly resistant to thermal degradation while providing a very high level of oxidation resistance. These desirable characteristics are supplemented by a high level of antiwear and corrosion inhibitors. Because of its unusual properties, Delvac 1 can continue to provide satisfactory lubrication without substantial deposits at temperatures up to 100 degrees above the threshold of operation of conventional mineral oils.

Delvac 1 carries an SAE 30 viscosity rating but behaves better than a conventional SAE 5W oil at very low temperatures. This is because the viscosity grades of automotive engine oils are developed according to definitions and test procedures developed by the Society of Automotive Engineers (SAE) for petroleum lubricants and not synthetic products. Thus, the SAE grade is indicative of fluidity only and does not define overall quality. As a result, the SAE viscosity grading system does not truly measure a product's viscosity-related engine performance. Where a conventional 5W oil does not flow properly at temperatures below 0°F, Delvac 1, because of the absence of wax crystals, remains fluid at subzero temperatures as low as -50°F.

Delvac 1 has all the advantages of an SAE 30 weight oil without the disadvantage of higher oil consumption inherent in multigrade oils using very light mineral oil base stocks. This is because its man-made molecules have higher boiling points than many of the molecules found in conventional oils. Delvac 1 does not evaporate as readily in the high-temperature piston ring area of highly turbocharged diesel engines at high operating temperatures.

At the high end of the temperature-viscosity scale, 210°F, Delvac 1 has essentially the same viscosity as most petroleum SAE 30 oils. However, because of its higher viscosity index and its unique molecular structure, it provides a better protective film than conventional oils over the full range of operating temperatures encountered.

Delvac 1 exceeds the zinc and phosphorous requirements of Ford ESE-M2C-144-A specification, International Harvester Fleet Service Newsletter IHC SLF 76-9, and Chrysler 09-14-77 Technical Service Bulletin. Delvac 1, in addition, conforms to the Detroit Diesel 7SE 270 (Rev. 10-76) specification.

TYPICAL CHARACTERISTICS

Typical physical and chemical characteristics of Mobil Delvac 1 synthetic engine oil are shown in the data sheet table:

Characteristics	Mobil Delvac 1
SAE No.	30
Gravity, API	30.7
Specific Gravity	.8724
Pour Point, °F	Below -65
Flash Point, °F	440
Viscosity	
cp at -40°F (CCS)	12,500
cp at 0°F (CCS)	1,200
cSt at 100°F	62.7
cSt at 210°F	10.3
cSt at 300°F	4.33
cSt at 400°F	2.72
cSt at 40°C	57.3
cSt at 100°C	10.08
SUS at 100°F	291
SUS at 210°F	60.3
Viscosity Index	164
Sulfated Ash, % wt.	.98
Total Base Number	7.0

APPLICATIONS

With Delvac 1, because of its unique long-lasting capabilities, over-the-road fleets, truck rental fleets, truck stops and owner/operators are able to extend drain intervals up to 100,000 miles in diesel-powered engines. Delvac 1 was also found to minimize filter deposits with the potential for longer filter usage. However, because of variables in filter quality and service conditions, the optimum filter change interval should be established in conjunction with the engine and filter manufacturers' guidelines. This should provide not only savings in maintenance costs and costs of oil, but also substantial savings in terms of equipment downtime. Delvac 1 will provide fuel savings of 2.0 to 5.6 percent, with up to 32 percent savings in oil make-up in over-the-road service. It can be shown that for a truck operating 100,000 miles per year, the savings in fuel economy, make-up, maintenance, and down-time will substantially outbalance the higher cost of lubricant per gallon and provide a substantial dollar savings per year for the fleet operator.

In pick-up and delivery and utility fleets, particularly gasoline-powered units, 25,000 miles without oil drain is feasible under optimum conditions with Delvac 1. Filter change intervals can be potentially extended to 25,000 miles or one year of service if filter quality and service conditions permit. Under these conditions, Delvac 1 is expected to provide fuel economy savings comparable to that obtained with diesel equipment, particularly in stop-and-go driving and in cold weather. Here, Delvac 1 is expected to provide maximum benefits in terms of reduced friction. In addition, because of its low volatility, the product would be expected to provide a make-up rate below that of conventional oil.

In utility fleets, particularly those that are used to repair telephone and electric lines in the winter, this type oil has demonstrated substantial reductions in the cost of batteries and electrical systems. The savings are compounded by substantial reductions in maintenance and repair expenses by eliminating road calls to start stalled engines in cold weather. Also eliminated is the use of high-watt block heaters. For diesel engines, idling time is reduced during periods on the road.

Off-the-road trucks used in the logging and mining industries under extreme weather conditions would be expected to benefit from Delvac 1 because of its ability to provide rapid cold startups and rapid warmups of the engine. Under these conditions the product provides good pumpability and good protective oil film which helps minimize wear under critical operating conditions.

In school bus fleets, refrigeration units, small 4-cycle engines, and in diesel service centers and units operating in Arctic subzero conditions, Delvac 1 should provide excellent low-temperature service — wherever an engine must operate at subzero temperatures.

In various tests, Delvac 1 generally far exceeded specification requirements. For example, in the API CD/SE and Mack EO-J specifications, Delvac 1 demonstrated its long-term quality retention characteristics by retaining its high performance level for twice the specified length in a "high-severity" Mack T-1 performance test. Its oxidation resistance ability was demonstrated in extended Sequence III C and CRC L-38 tests. Alkalinity retention was demonstrated in the extended Mack T-1 test, while high temperature detergency was illustrated in the "high-severity" Mack T-1 and in the Mack T-5, and Caterpillar 1-G tests.

Delvac 1 further demonstrated its long-term performance capabilities in additional tests. For example, copper/lead corrosion protection was shown in extended CRC L-38 tests, sludge protection was shown through extended-duration Sequence VC tests. High-temperature oxidation resistance was demonstrated in long-term Mack and Cummins field tests and Oldsmobile gasoline VC tests.

Delvac 1 is miscible in and fully compatible with conventional mineral oils. It also provides outstanding foam protection and is compatible with all seals currently found in heavy-duty diesel and gasoline engines in truck fleets. No system preparation other than proper draining and installation of a new filter is required when Delvac 1 is used in an engine for the first time. Under emergency circumstances, conventional oils can be used as make-up for Delvac 1, but this mixing may result in some degradation of the performance properties of Delvac 1.

Even under the most severe winter conditions, dilution of the crankcase oil with gasoline or kerosine prior to shut-down is unnecessary and should not be practiced when Delvac 1 is in use. The addition of the diluent will not materially improve the cold cranking and may have an adverse effect on the performance of Delvac 1.

ADVANTAGES

Mobil Delvac 1 synthetic engine oil offers the following advantages and benefits:

- Reduced fuel consumption, 2.0 to 5.6 percent over conventional oils.
- Improved cold temperature cranking.
- Extended drain capability: potentially 100,000 miles for diesel engines, and 25,000 miles for gasoline engines.
- Reduced lube oil consumption: up to 32 percent less make-up oil.
- Improved equipment availability.
- Reduced engine wear.
- Improved engine cleanliness.
- Longer battery life, with reduced starting and electrical system costs.
- Improved truck acceleration.
- Improved energy conservation.
- Full compatibility with mineral oils.
- Full compatibility with engine seals.
- Reduced oil sump temperatures.
- Lower engine friction properties

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Mobil

Facts about Synthetic Lubricants

The production of synthetic lubricants starts with synthetic base stocks which are often manufactured from petroleum. The base fluids are made by chemically combining (synthesizing) low molecular weight compounds with adequate viscosity for use as lubricants. Unlike mineral oils, which are a complex mixture of naturally occurring hydrocarbons, synthetic base fluids are man-made and tailored to have a controlled molecular structure with predictable properties.

Synthesized base fluids may be classified as follows:

- **Synthesized Hydrocarbons**
Olefin Oligomers
Alkylated Aromatics

- **Organic Esters**
Dibasic Acid Esters
Polyol Esters

- **Other**
Polyglycols
Phosphate Esters
Silicates
Silicones
Polyphenyl Ethers
Fluorocarbons

- **Blends**
Mixtures of above
(May also contain minor amounts of mineral oil.)

Six of the base fluids — olefin oligomers, alkylated aromatics, dibasic acid esters, polyol esters, polyglycols, phosphate esters — account for more than 90 percent of the total synthetic lubricants used worldwide. Because of their importance, these base fluids are detailed in the remainder of this bulletin.

Synthesized Hydrocarbon Fluids

Mobil's SHF (synthesized hydrocarbon fluids) base stocks are olefin oligomers synthesized from specific olefins by a controlled polymerization process. The result is a fluid composed of hydrocarbons with a similar molecular structure.

Since the preferred chemical structures can be selected and controlled by processing, the synthesized hydrocarbon fluids are almost entirely paraffinic, giving a much greater degree of stability than fluids with aromatic or naphthenic ring structures. Also, because undesirable waxy materials are absent, very low pour points are achieved.

Properly formulated lubricants based on synthesized hydrocarbon fluids have six noteworthy advantages compared with high quality mineral oil lubricants:

1. Excellent viscosity/temperature properties and shear stability — provides improved wear protection.
2. Good high temperature oxidation stability — reduces deposit formation. Typically, the upper operating limit for SHF lubricants is 50 degrees higher on the Celsius scale (100 degrees on the Fahrenheit scale) than the maximum temperature for high quality mineral oils.
3. Good low temperature characteristics (pour point -55°C [-67°F]) — improves cold weather flow properties.
4. Compatible with mineral oils — no special system design required.
5. Long service life — 3 to 5 times better than the best mineral oils.
6. Low volatility — reduces consumption.

A line of aviation, automotive and industrial lubricants using SHF base stocks has been developed by Mobil — many with the registered brand identification of Mobil SHC as shown in the following table:

Mobil's SHF Lubricants

Mobil Brand	Major Applications
Mobil SHC	ID resale motor oil
Mobil 1	Resale motor oil
Mobil Delvac SHC	Commercial engine oil
Mobil Delvac 1	Commercial engine oil
Mobilube SHC	Arctic gear lube
Mobilgrease 28	Wide temperature grease for Industrial use
Mobil SHC 624	Broad temperature industrial circulation systems & gears
Mobil SHC 626	
Mobil SHC 629	
Mobil SHC 630	
Mobil SHC 634	High temperature calenders & worm gears
Mobil SHC 639	High temperature calenders
Mobil SHC 824	Nuclear power plants &
Mobil SHC 825	stationary gas turbines
Mobil SHC 1126	High temperature conveyors

The value and performance advantages of these lubricants has been proven and their worldwide availability is expanding.

Organic Esters

These are either dibasic acid or polyol types. Dibasic esters, frequently called diesters, have assets that include a shear stable viscosity over a wide temperature range (-75°C to 205°C, -103°F to 401°F), high film strength good metal wetting, and low vapor pressure at elevated temperatures. Another asset is good additive acceptability enhancing their use in compounded crankcase oils and in selected commercial lubricants. Mobil markets diesters in combination with SHF in a number of the Mobil SHC products. Mobil is currently marketing a line of diester industrial lubricants for use in rotary screw and vane compressors and in some reciprocating types.

Polyol esters, which were developed later than diesters, have many of the same performance advantages and extend the service temperature to higher levels. Their principal use is in aviation turbine oils, such as Mobil Jet Oil II.

Phosphate Esters

These inorganic esters, used with carefully selected additives in the Mobil Pyrogard 50 Series, replace mineral oils where their combustibility may be a hazard. Pyrogard 50 series provides performance balanced, fire resistant fluids for use in hydraulic and circulation systems.

The comparative temperature limits of mineral oil and synthetic based lubricants are shown in the chart below. Suggested markets for Mobil's synthetic lubricants in automotive, industrial, and aviation services are itemized in the adjacent tabulation. For more complete product information, please refer to Product Data Sheets for individual products.

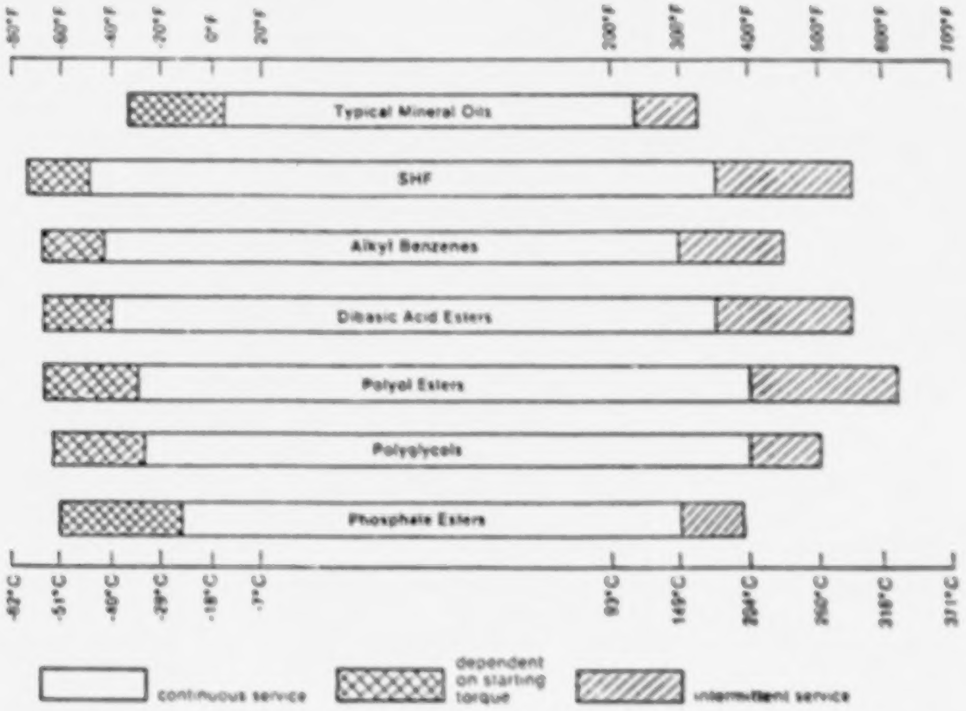
Mobil's Polyglycol Lubricants

Brand	Major Applications
Mobil Glygoyle 11*	Heat transfer systems, compressors, natural gas valves, LPG screw compressors and severe duty bearings and gears
Mobil Glygoyle 22 Mobil Glygoyle 30	Severe duty bearings, gears, and compressors
Mobil Glygoyle 80	R-12 refrigerant screw compressors and severe duty bearings, gears and compressors

*Available in International Division only.

Polyglycols

Polyglycols were one of the first synthetic lubricants. They are more accurately described by the name polyalkylene glycols and are among the least expensive and most commonly used synthetic fluids. Primarily, they are obtained from petroleum and are high molecular weight polymers of ethylene or propylene oxides or both. Polyglycols have excellent viscosity/temperature properties and are used in applications from -40°C to 205°C (-40°F to 401°F) and have low sludge buildup. Mobil branded polyglycols are shown in the above tabulation.



Comparative Temperature Limits — Mineral Oil and Synthetic Lubricants

Mobil's Synthetic Lubricants — Market/Application

Equipment Type — Lubricated Unit	Operating Conditions	Premium Lubricant Recommendations Mineral Oil	 Synthetic	Advantages of Synthetic Oils
Industrial				
Calenders — Rubber, Plastics, Board, Tile	High temperature 180°C to 260°C (356°F to 500°F)	Mobil D.T.E. AA, HH, KK	Mobil SHC 634, 639 Mobil Glygoyle 22, 30	Extended service, reduced deposits, oxidation and thermal cracking.
Paper Machines — Dryers, Calenders, Drive Gear Units	High temperatures	Mobil D.T.E. Ex Hvy, BB; Mobil Paper Machine Oils	Mobil SHC 634 Mobil Glygoyle 22, 30	Extended service, reduced deposits, oxidation and thermal cracking.
Nuclear Power Plants — Vertical Coolant Motors, 6-9000 hp	Annual oil change 8000 hours min.	Mobil D.T.E. Medium	Mobil SHC 824	Extended service, reduced deposits.
Gas Turbines — Small Standby, Commercial	Ambient -55°C to 60°C (-65°F to 140°F)	Mobil D.T.E. 797, Light, Medium	Mobil SHC 824, 825	Extended service, broader temperature range of application, reduced deposits.
Steam Turbines — Electro-Hydraulic Control, Throttle/Governor	Near superheated steam lines	Mobil D.T.E. 797, Light, Medium, Heavy Medium	Mobil Pyrogard 53 Mobil Pyrogard 53T*	Fire resistant.
Tenter Frame & High Temperature Conveyors — Bearings	150°C to 260°C (302°F to 500°F)	Mobil Etna Oil No. 6 Mobil Oven Conveyor Lubricant	Mobil SHC 1126	Reduced deposits and improved wear protection.
Enclosed Gears — Parallel, Worm, Spur, Bevel	Heavy duty, shock loaded, severe service	Mobilgear 600 Steam Cylinder Oils	Mobil SHC 600 Series, Mobil Glygoyle 22, 30	Extended service, better oxidation resistance at elevated temperatures.
Refrigeration Compressors — SRM License Screw Compressors	Severe service	Gargoyle Arctic Oil Series	Mobil SHC 626 Gargoyle Arctic SHC 224, 226 Mobil Glygoyle 11, 22, 30, 80	Improved efficiency.
Metal Diecasting Hydraulic Systems	Molten metal, source of ignition	Mobil D.T.E. 20 Series	Mobil Pyrogard 50 Series	Fire resistant.
Mining — Continuous Miners & Associated Equipment	Fire hazards exist	Mobil D.T.E. 20 Series Mobil Pyrogard D	Mobil Pyrogard 53 (Pyrogard D alternate where preferred)	Fire resistant.
Primary Metals — Slab, Continuous Casters, Rolling Mills, Shears, Ladles, Furnace Controls	Fire hazards exist	Mobil D.T.E. 20 Series	Mobil Pyrogard 53 (Pyrogard D alternate where preferred)	Fire resistant.
Air Compressors	Severe service	Mobil Rarus 400, 300 Series	Mobil Rarus 800 Series	Extended service, reduced deposits.
Automotive				
Passenger Car Gasoline Engines	Severe start-stop driving	Mobil Super 10W-40 15W-30	Mobil 1 Mobil SHC 10W-50, 15W-50	Improved fuel economy, low temperature starting, oil economy, and wear protection.
Truck & Off Highway Gas & Diesel Engines	Arctic or subzero	Mobil Delvac Special or Mobil Heavy Duty 5W†	Mobil Delvac SHC* Mobil Delvac 1	Improved low temperature starting and operation, longer drain interval, and fuel and oil economy.
Trucks & Cars, Drive Axles & Manual Transmissions — Hypoid, Spiral Bevel & Spur Gears	Mild to severe	Mobilube HD 75W*	Mobilube SHC 75W-90	Improved low temperature starting and operation, and wear protection.

* Available in International Division only.
† SAE 5W-20.

Mobil's Synthetic Lubricants — Market/Application (Cont.)

Equipment Type — Lubricated Unit	Operating Conditions	Premium Lubricant Recommendations Mineral Oil	 Synthetic	Advantages of Synthetic Oils
Aviation — Military & Commercial				
Commercial Turbine Engines — Pratt & Whitney; Allison; G.E.; Rolls-Royce Avon, Gnome, Spey and Viper-MIL-L-23699A approved	Temperature to 220°C (428°F)	None	Mobil Jet Oil II	Broad temperature range of service, high temperature stability.
Military Turbine Engines — MIL-L-7808H approved	Temperature to 190°C (374°F)	None	Avrex S Turbo 256	High temperature stability.
Aircraft, All — Wheel Bearings, Wing Flap Screws — MIL-G-81322B approved	Temperature -55°C to 180°C (-67°F to 356°F)	None	Mobilgrease 28	Broad temperature range of service, high temperature stability.

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Chevron

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MAY 17 1979
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May 8, 1979

Mr. Thomas M. Baines
U.S. Environmental Protection
Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105

Dear Mr. Baines:

You recently spoke with Mr. K. L. Kipp and Mr. R. O. Bolt concerning Chevron engine lubricants suitable for heavy-duty engines. At your request, we are sending one-quart samples of the engine oils listed in the attached table to Dr. David Fine, New England Institute of Life Sciences.

I am enclosing copies of Chevron Teknifaxes which describe these products in more detail. Please let me know if you have any further questions.

Very truly yours,

R L Courtney
R. L. Courtney

RLC:ccp
Encl. - Table I
Four Chevron Teknifaxes

100 Years Helping to Create the Future

TABLE I

CHEVRON DELO FLEET ENGINE LUBRICANTS

Engine Lubricant	1978 Relative Sales Volume[1]	API Performance Category	Typical Compositional Data[2]		
			N₂, Wt %	Sulfated Ash, Wt %	Zinc, Wt %
Chevron Delo 100 Motor Oil SAE Viscosity Grade 10W, 20W-20, 30, 40, 50	3.0	CC	0.03	0.74	0.1
Chevron Delo 200 Motor Oil SAE Viscosity Grade 10W, 20W-20, 30, 40[3]	1.0	CC,CB,SE,SD	0.01	0.98	0.11
Chevron Delo 300 Motor Oil SAE Viscosity Grade 10W, 20W-20, 30, 40	1.3	CD	0.03	1.25 (1.5 for SAE 10W Only)	0.13 (0.16 for SAE 10W Only)
Chevron Delo 400 Motor Oil SAE Viscosity Grade 10W, 20W-20, 30, 40, 50	3.1	CC,CD,SE,SD	0.17	0.98	0.13
Chevron Delo 400 SAE 15W-40	0.2	CC, CD, SE	0.20	0.98	0.13

[1] Sales relative to Chevron Delo 200 Motor Oil and Chevron Special Motor Oil (all viscosity grades combined).

[2] See Chevron Teknifax for additional information.

[3] Includes Chevron Special Motor Oil volume.

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Typical test data

SAE GRADES	10W	20W-20	30	40	50
GRAVITY, °API	29.8	28.6	27.6	27.2	26.5
VISCOSITY					
Poises at 0°F	17.5	73.0	–	–	–
Kinematic, cSt					
at 210°F	6.1	9.1	12.4	15.5	20.1
SSU at 100°F	182	363	615	857	1275
SSU at 210°F	46.2	56.1	67.9	79.9	98.5
VISCOSITY INDEX	90 – 110				
POUR POINT, °F	–20	–15	0	+10	+10
FLASH, °F	405	445	470	480	500
COLOR	5.0	5.0	5.5	6.0	3.0 (DIL)
ASH (SULFATED), WT. %	0.7	0.7	0.7	0.7	0.7
ZINC, WT. %	0.1	0.1	0.1	0.1	0.1

The test data shown in this table are average values only. Minor variations which do not affect product performance are to be expected in normal manufacturing. Please see your Chevron representative for more details.

NOTE:

Chevron Delo 100 Motor Oil darkens rapidly in use. This is a sign of the high dispersancy of the oil. It shows the superior ability of the product to disperse sludge-like materials. It is the result of the excellent dispersion of sub-micronic sludge particles, which other oils may allow to agglomerate and deposit in the engine or filter.

Chevron Delo 200 Motor Oils

What type of oils are they?

Chevron Delo 200 Motor Oils are premium quality automotive crankcase oils designed for gasoline engines in severe service and for diesel engines in moderate to severe duty. Therefore, they are ideally suited for mixed fleet service.

They are manufactured from 100% solvent refined, paraffinic base oils, selected for their low carbon-forming characteristics, high viscosity index and maximum oxidation stability. To these stocks, a carefully balanced additive package is added. This treatment consists of dispersant, detergents, anti-wear and extreme-pressure agents, oxidation and corrosion inhibitors and an effective foam inhibitor.

Where should they be used?

Chevron Delo 200 Motor Oils are recommended for:

1. Mixed fleets of automotive gasoline and diesel engines where the manufacturers require oils for API Services SE or CC. The requirements are often specified as MIL-L-46152 (SE and CC) or MIL-L-2104B (CC).
2. Mobile and stationary engines in industrial, agricultural and marine applications requiring the use of this type of lubricant.
3. Engines from more than 50 domestic and foreign manufacturers.
4. Engines which require an oil meeting A.P.I. service classifications CC and SE.
5. Hydraulic systems where engine oils are recommended.

How do they perform?

Chevron Delo 200 Motor Oils provide outstanding control of deposits and wear over a wide range of operating conditions.

Highly effective additives are selected to enhance the desirable properties of the quality base oils. Here is how the finished lubricants do the jobs assigned to them:

1. High temperature protection against oil oxidation and thickening. Varnish formation on pistons, carbon build-up in ring grooves, and deposits on other engine parts are kept to safe, low levels.
2. Low temperature protection against sludge formation. Oil screens, valve train chambers, and other engine parts are kept cleaner in low temperature or stop-and-go operation.
3. Rust and corrosion protection against the water and acids formed by condensation, combustion by-products or oil oxidation. Bearings and other engine surfaces are protected by barrier films and neutralization of metal-eating contaminants. In fact, running an engine for five minutes on a fresh charge of Chevron Delo 200 will give sufficient protection for seasonal layup.
4. Protection against wear and scuffing. Special additives guard against piston scuffing and abnormal wear of parts subjected to extreme pressures, such as valve train wear points.
5. Improved engine efficiency. Pre-ignition causing deposits are reduced; positive crankcase ventilation systems are kept cleaner.

6. Longer filter life. Most oil-insoluble contaminants are kept so finely dispersed by the oil that they pass right through the filter medium.

This leaves the filter more time to trap larger, harmful contaminants. Filter change intervals are extended accordingly.

Chemically treated filters interfere with the oils ability to suspend submicronic particles and are not required.

The immediate darkening of Chevron Delo 200 Motor Oils in use is normal and should be expected. This is evidence of their superior ability to disperse contaminants and keep engines clean.

Qualifications met

Chevron Delo 200 Motor Oils meet the specific requirements of the following:

Diesel Engines—API Service CC
- Allis-Chalmers—Naturally aspirated engines in mild duty.
- Caterpillar—Naturally aspirated engines under reduced drain periods.
- Cummins—Naturally aspirated engines.
- Detroit Diesel—Single viscosity grades only.
- International—Naturally aspirated engines.
- Mack-Naturally aspirated engines (EO-H).

Gasoline Engines—API Service SE
- American Motors
- Chrysler Corporation
- Ford ESE-M2C101-C & ESE-M2C144-A
- General Motors GM 6136-M

Typical test data*

SAE Grade	Poises	Viscosity cST (SUS)		Viscosity Index	Pour Point		Flash Point		Sulfated Ash	Zinc	
	18°C	40°C	100°C		°C	(°F)	°C	(°F)	Wt. %	Type	Wt. %
10W	24	44 (205)	7 (48)	105	−34	(−29)	207	(405)	0.9	Alkyl	0.11
20W 20	57	71 (330)	9 (56)	100	−27	(−19)	235	(455)	0.9	Alkyl	0.11
30	–	116 (538)	12 (67)	93	−19	(−5)	252	(485)	0.9	Alkyl	0.11
40	–	160 (740)	15 (78)	92	−18	(−2)	254	(490)	0.9	Alkyl	0.11

*Subject to change without notice

Chevron DELO 300 Motor Oil

(Formerly Chevron RPM DELO 300 Motor Oil)

Description

Chevron Delo 300 Motor Oil is a Caterpillar approved Series 3 Oil. It also satisfies the requirements of the former Military Specification MIL-L-45199B. The product is manufactured from solvent refined paraffinic base oils having high viscosity index and low carbon-forming characteristics.

The special detergents and other additives used keep engine parts clean, particularly in the area of the ring belt, piston skirt and valve surfaces. As a result they minimize both low and high temperature deposits and those ash deposits that caure valve "wheezing" in certain turbocharged diesel engines. The additives also help to control the harmful effects in the engine caused by using high-sulfur fuels.

Chevron Delo 300 Motor Oil contains corrosion inhibitors which minimize the formation of corrosive acids and form protective films on bearings and all lubricated surfaces. Effective defoaming and extreme pressure additives are used to satisfy the requirements of a good hydraulic oil, as well as providing protection for engines and gear cases.

Typical applications

Chevron Delo 300 Motor Oil was developed and is recommended for use in diesel engines operating under very severe service conditions where a Series 3 Oil is required for a particular make of engine. It has also given excellent service in gasoline engines. This oil is a solution for an operator who wishes to use a Series 3 Oil in a variety of types and makes of engines.

It is specifically suited for use in Caterpillar and other heavy duty engines operated by:

1. Contractors
2. Miners
3. Farmers
4. Truckers
5. Loggers
6. Stationary engine installations
7. Marine installations

It also gives excellent performance in:

1. Hydraulic systems.
2. Gear cases, when motor oil is recommended by the manufacturer.
3. Engines requiring an oil recommended for API Service Classification CD.
4. Engines requiring an oil meeting the requirements of the former Military Specification MIL-L-45199B.

Performance qualities

The performance qualities of Chevron Delo 300 Motor Oil have been proven in laboratory and field tests. Benefits shown for the new oil include:

Minimizes deposits –
Minimizes ring sticking problems, and controls deposits in both high and low temperature services.

Minimizes wear –
Contains effective anti-wear agent, neutralizes acids, and solublizes acidic material to prevent corrosive wear.

Extends valve life –
Low ash feature controls valve wheezing.

Oxidation stability –
Exceptionally resistant to oxidation.

Rust inhibited –
Protects all metal surfaces under the most difficult conditions of equipment operation and storage.

Long oil filter life –
The high dispersancy of the oil assures long life of oil filters, allowing the oil filter to be more effective in filtering out abrasive materials.

Engine field tests

Field tests were conducted in over 170 diesel and gasoline engines in construction equipment and in more than one million miles of over-the-road heavy duty trucking.

In addition to extensive testing in all the most popular makes of diesel engines in contractor-type service, Chevron Delo 300 Motor Oil was also field tested and proven in popular make truck engines selected because they had a high detergent requirement and were high output engines. Improvements were obtained with respect to deposit control, wear and valve condition with Chevron Delo 300 Motor Oil as compared with a quality conventional Series 3 reference oil.

To test the ability of Chevron Delo 300 Motor Oil to solve operational problems including valve "wheezing," a field test location was selected where the operating conditions and equipment involved were known to present a serious problem. Units were changed to the low-ash Chevron Delo 300 Motor Oil with outstanding results.

The improvements designed into Chevron Delo 300 Motor Oil add up to many thousands of trouble-free engine hours (or miles) and low operating costs.

TYPICAL TEST DATA

SAE GRADE	10W	20/20W	30	40
GRAVITY °API	28.0	27.5	27.0	26.5
FLASH POINT, °F	395	440	465	475
VISCOSITY				
AT 100°F, SUS	196	365	590	775
AT 100°F, CS	42.02	78.75	127.4	167.2
AT 210°F, SUS	47.0	56.5	68.5	78.5
AT 210°F, CS	6.35	9.21	12.56	15.14
VISCOSITY INDEX	95 – 110			
POUR POINT, °F	–25	–10	0	+10
SULFATED ASH, WT. %	1.5	1.2	1.2	1.2
ZINC, WT. %	.16	.13	.13	.13

The test data shown in this table are average values only. Minor variations which do not affect product performance are to be expected in normal manufacturing. For more details, see your Chevron representative.

NOTE: Chevron Delo 300 Motor Oil darkens rapidly in use as the result of the excellent dispersion of sub-micronic sludge particles in the oil. This is a sign of the superior ability of the product to disperse sludge particles which other oils may allow to agglomerate and deposit in the engine or filter.

Package sizes generally available

Chevron Delo 300 Motor Oil is available in: 1-Quart Cans; 5-Gallon Pails; 55-Gallon RSB's.

Chevron Delo 400 Motor Oil

Description

When introduced to the marketplace in 1971, Chevron Delo 400 Motor Oil was the first oil to: (1) satisfy the full requirements of all major makes of automotive diesel engines, (2) meet the requirements of all domestic brands of gasoline engines, and (3) meet the requirements of the most recent military specifications, MIL-L-2104C and MIL-L-46152.

Subsequent to its introduction, several engine manufacturers changed their specifications for the oils to be used in the crankcases of the engines they build.

In addition, it has become desirable for users to extend periods between engine oil drains in order to conserve oil, to reduce environmental problems and to reduce costs.

The improved Chevron Delo 400 Motor Oil meets all of the latest requirements of all of the major automotive engine builders, and allows for extending intervals between drains.

Chevron Delo 400 Motor Oil contains only alkyl type zinc dithiophosphates as specified by several engine builders. This zinc compound provides excellent anti-wear protection.

Typical Applications

Chevron Delo 400 Motor Oil is a multi-application oil recommended for use in all major automotive type diesel and gasoline engines in all types of service. It is particularly recommended for use in fleets containing different types of engines made by several manufacturers.

Qualifications

Chevron Delo 400 Motor Oil meets the warranty requirements of the following engine manufacturers:

Diesel Engines

- Caterpillar Tractor Company
- Cummins Engine Company
- Detroit Diesel Allison Division, General Motors Corp.
- International Harvester Company
- Mack Trucks, Inc. (EO-H and EO-J)

Gasoline Engines

- American Motors Corp.
- Chrysler Corporation
- Ford Motor Company (ESE-M2C-144A)
- General Motors Corp. (Standard 6136M)
- International Harvester
  - Mack
  - White

Chevron Delo 400 Motor Oil meets the requirements of the following API Engine Service Classifications:

CC, CD, SE

Chevron Delo 400 Motor Oil has been tested in its most popular grade which meets the requirements of the following current military specifications: MIL-L-2104C and MIL-L-46152. It also meets Allison Type C-3 and Vickers hydraulics performance in Grade SAE 10W.

Field Experience

Chevron Delo 400 Motor Oil is in use in hundreds of automotive fleets nation-wide. It has given outstanding performance in trucks and automobiles of all makes for many thousands of millions of miles over several years.

Performance Qualities

The performance qualities of Chevron Delo 400 Motor Oil have been proven in laboratory and field tests. The benefits of this oil include:

General Use

This one oil can be used in all major automotive type diesel and gasoline engines in all types of service. As a result, crankcase oil inventory is minimized and the problem of getting the wrong oil in an engine is eliminated. It is recommended for use in transmissions and hydraulic systems requiring a fluid meeting the Allison Type C-3 in Grade SAE 10W or Caterpillar TO-2 specification, SAE 30.

Minimum Deposits

Ash deposits in the combustion chamber area and on valve surfaces are minimized. Sludge, varnish and carbonaceous deposits are controlled to extend engine life.

Minimum Wear

An effective anti-wear agent neutralizes acids and solubilizes acidic material to reduce corrosive wear to a minimum.

Extended Drain Intervals

The initial alkalinity (acid neutralizing ability) of Chevron Delo 400 Motor Oil (9TBN by ASTM D-2896) is among the highest in motor oils for use in trucks and automobiles.

Under most operating conditions, drain intervals can be extended and the oil will still provide excellent protection for the engine parts when Chevron Delo 400 Motor Oil replaces the more conventional type universal motor oils.

The optimum oil drain interval can best be determined by a used oil monitoring system and a good engine maintenance program.

Oxidation Stability

Exceptionally resistant to oxidation.

Rust Inhibited

Protects metal surfaces under the most difficult conditions of equipment operation and storage.

Low Temperature and High Temperature Operation

Provides top performance in engines operating in both low and high temperature service.

Long Filter Life

The high dispersancy of the oil extends the life of oil filters, allowing the oil filter to be more effective in filtering out abrasive materials.

TYPICAL TEST DATA

SAE Viscosity Numbers	10W	20W-20	30	40
Viscosity				
At 100°F, SUS	217	328	538	757
At 100°F, cSt	46.5	70.7	116	163
At 210°F, SUS	49.1	55.8	66.9	79
At 210°F, cSt	7.0	9.0	12.2	15.3
Viscosity Index	95-110			
Flash Point, °F (Min)	400	410	425	450
Pour Point, °F	-25	-10	-5	5
TBN (ASTM-2896)	9	9	9	9
Sulfated Ash, Wt. %	0.98	0.98	0.98	0.98
Zinc, Wt. % (Alkyl)	0.13	0.13	0.13	0.13

NOTE: The test data shown in this table are average values only. Minor variations which do not affect product performance are to be expected in normal manufacturing. For additional information please see your Chevron representative.

E-42

MACK TRUCKS, INC.
One of the Signal Companies
1999 Pennsylvania Avenue, Hagerstown, Maryland 21740

September 6, 1979

Area Code (301) 733-8300

Ms. Ulku Goff
New England Institute of Life Sciences
125 Second Avenue
Waltham, MA 02154

Dear Ms. Goff:

Under separate cover we are forwarding new and used engine oil samples from two different Mack engines, ETZ675 and ETAZ676, used in highway service. We understand these samples will be used for an EPA nitrosamines study.

One pint (four four-ounce plastic containers) of new oil, used oil at 75 hours, used oil at 150 hours and used oil at a complete oil change are included for each engine. Both vehicles are using exactly the same new oil so only one sample of new oil is included.

Also included are the used oil data with each sample, and the other data requested are attached.

Should you require additional information please contact me.

Very truly yours,

L. T. Murphy

L. T. Murphy
Project Engineer
Technical Support Lab

dk

Attachment

It's part of the language... *"Built Like a Mack Truck"*

VEHICLE INFORMATION FOR EPA NITROSAMINES STUDY

MACK UNIT NUMBER	211	212
VEHICLE TYPE	R685ST	
MAIN USE	OVER-THE-ROAD	
MODEL YEAR	1968	
MODEL SIZE	TANDEM AXLE	
CONFIGURATION	CONVENTIONAL	
USUAL TRIP LENGTH (MILES)	315/DAY	315/DAY
TOTAL MILES ON VEHICLE	681,683	353,959
ENGINE MODEL	ETAZ676	ETZ675
DISPLACEMENT	672 in^3	
HORSEPOWER	285	235
CONFIGURATION	HIGH TORQUE RISE (MAXIDYNE)	
ASPIRATION	TURBOCHARGED/INTERCOOLED	TURBOCHARGED
TOTAL MILES ON ENGINE	121,358	60,174
ENGINE MILES AT START OF TEST	121,358	60,174
MAINTENANCE INTERVAL (MILES)	25,000	16,000
FUEL USED	EXXON 260	
OIL BRAND NAME	MOBIL INFILREX 205	
OIL ADDITIVE	EXXON CHEMICAL ECA7320 (.1% NITROGEN)	
AVERAGE OIL CONSUMPTION (MI/QT)	800	700
AVERAGE FUEL CONSUMPTION	5.4	5.4

DEUTZ
DIESEL (CANADA) LTD
RESEARCH AND DEVELOPMENT DIV

Montreal, May 30th, 1979

Mr. Thomas Baines
Emission Control Technology Division
U.S. Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105

Ref.: Diesel Crankcase Emissions Characterization Program

Dear Tom,

As we confirmed to you in the past, Deutz, in conjunction with other EMA companies, is interested in participating in EPA's Diesel Crankcase Emissions Characterization Program.

For that purpose, a total of 4 oil samples (sample volume = 1 litre each) will be submitted to the New England Institute of Life Sciences:

Sample No. 1 : Old oil, prior to oil change.
Sample No. 2 : Fresh oil, from drum.
Sample No. 3 : Used oil, with approx. 75 service hours.
Sample No. 4 : Used oil, with approx. 150 service hours.

Additional information on the samples are given in Attachment No. 1.
The samples will be obtained from an engine installed in our field test vehicle.

The following information should contribute to a better evaluation of the oil analysis results:

1. Vehicle Specifications

Truck: Ford LN 8000 tractor
Weight: 5700 kg
Rear Ratio: 6.14

Trailer: RAM
Length: 8.10 m (27 ft.)

GVWR (truck and trailer): 16 602 kg (36 600 lbs).

........../2

4660 HICKMORE AVE., MONTREAL, QUE., CANADA H4T 1K2 TLX:05-825773 (514)735-44

2. Vehicle Usage

The following are average values:

Service Type: 90% on-highway, 10% city
7 hours per shift
450 - 500 km per shift

The vehicle runs 5 days per week on a 2-shift per day basis. It accumulates approximately 70 hours per week = 5 000 km (3120 miles) per week.

3. Engine Specifications

Engine Type	F8L 610
Displacement:	6544 cm^3 (400 in^3)
Power Output:	160 HP
At Rated Speed:	3600 min^{-1}
Number of Cylinders/Arrangement:	8-V
Method of Aspiration:	Naturally aspirated
Combustion Cycle:	4 stroke, diesel direct injection
Engine Cooling:	Air-cooled
Exhaust Gas Recirculation:	No
Crankcase Ventilation:	Open to atmosphere through an oil separator.
Lube Oil System Capacity (including oil filter):	14 ℓ (3.7 US gall.)

The engine belongs to a new engine family development work done at our Research and Development Centre located in Montreal, Canada. Since this work is still in progress, the engines are not yet EPA certified, but covered by EPA's Testing Exemptions and CARB's Experimental Permits.

The engine was installed in the vehicle in July 1978. Some engine components were replaced since then (Reasons: Components re-design, parts failures, etc.). No engine re-build or major repair has been performed. A detailed engine inspection was carried out in February 1979, at which opportunity some components (liners, pistons, etc.) were cleaned and re-installed.

As of May 21st, 1979, the engine has accumulated a total of 1960 service hours in the vehicle (592 service hours since inspection in February, 1979), corresponding to 111 542 km (69 714 miles).

........../3

4. Oil

For a long period of time, all engines at our Research and Development Centre ran with Rotella T 30 oil supplied by Shell (Canada). Approximately 12 months ago, Shell (Canada) changed the oil denomination to Rotella S 30.

According to Shell, the oil Rotella S 30, available in Canada, corresponds to Rotella T 30, available in the U.S.A. The exact differences between these oils, if any, is proprietary information to Shell, and cannot be released to customers. Both oil types are classified as SE, CC as per A.P.I. requirements.
Shell Rotella S 30 (Canada) has a Nitrogen concentration of ≥ 0.21% (mass).

5. Oil Change Intervals

During the field testing program, oil changes are performed each 180 - 200 service hours, or approximately each 15 000 km (≈9 375 miles).

6. Oil Consumption

The first engines built for the purpose of endurance testing of major components did not include an optimized liner/piston/ring package and consequently exhibited high oil consumption. The field test vehicle is powered by one of these engines. Its oil consumption level, averaging 6 litres/1000 km (2.5 US gall./1000 miles) is several times higher than the present development engines running in test cells.

7. Fuel

The fuel used by the engine is a commercially available Diesel fuel, bought from Gulf at their service stations.
No additives are added to the fuel by Deutz.

We hope that this information will contribute to your evaluation of the oil analysis results. We are looking forward to the opportunity of sharing your results with us, and the other EMA members.

Should you need additional historical data in terms of vehicle/engine usage, please do not hesitate to contact us.

Sincerely yours
DEUTZ DIESEL (CANADA) LIMITED

Sauerteig

E. Sauerteig
Supervisor
Combustion and Emission Development

BCC.:
Mr. Vossmeyer
D, DT, DD, P. Wuensche
AS-TI, AS-TGV

ES/ghc/D8/Enclosure

ATTACHMENT NO. I

SAMPLE No. 1

Oil removed from the engine sump during oil change.
Following parameters apply to this "old" oil:

1. Date of oil change: May 21, 1979
2. Oil type: Shell (Canada) Rotella S 30
3. Total service hours in the sump: 166
4. Total time in the sump: 21 days
5. Distance driven by the vehicle during that time: 11 035 km (6 897 miles)
6. Oil quantity added during that time: 68.5 litres (18.1 US gal.)
7. Oil consumption during that time: 6.2 ℓ/1000 km (2.6 US gal/1000 miles)

SAMPLE No. 2

New oil refilled to engine sump.

1. Date of refill: May 21, 1979
2. Type of oil: Shell (Canada) Rotella S 30
3. Amount of oil refilled: 14 ℓ (3.7 US gal.)
4. Oil filter replaced: Yes

Samples No. 1 and 2 were stored in a refrigerator until shipment, on May 25th, 1979.

SAMPLE No. 3

At the requested interval, the third sample was collected.

1. Date of sampling: May 30, 1979
2. Oil type: Same as sample no. 2
3. Total service hours in sump: 75.5
4. Total time in sump: 9 days
5. Distance driven by the vehicle during that time: 5 043.7 km (3 152.3 miles)
6. Oil quantity added during that time: 34.6 litres (9.14 US gal.)
7. Oil consumption during that time: 6.68 ℓ/1000 km (2.9 US gal./1000 miles)

Sample no. 3 was stored in a refrigerator until shipment on June 4, 1979.

........../2

SAMPLE No. 4

Following data applies to the fourth and last sample:

1. Date of sampling: June 7, 1979
2. Oil type: Same as sample no. 2
3. Total service hours in sump: 154.2 litres
4. Total time in sump: 18 days
5. Distance driven by the vehicle during that time: 10034.5 km (6271.6 miles)
6. Oil quantity added during that time: 64.9 litres (17.14 US gal)
7. Oil consumption during that time: 6.47 ℓ/1000 km (2.7 US gal//1000 miles)

Sample no. 4 was stored in a refrigerator until shipment on June 11, 1979.

ES/ghc/D8
04-06-1979

Appendix F

The Results of the Used Oil Samples Acquired by New England Institute for Life Sciences

Sample No.	Type of Oil	Type of Engine	Miles on Oil	DMN (ppb)	
				GC	HPLC
1	Gulf 30W	Detroit Diesel 6-71	7,000	0.60	0.60
2	Gulf 30W	Detroit Diesel 6-71	8,975	0.95	0.70
3	Chevron Delo 400, SAE30	Mack Diesel 6-76	6,000	1.50	1.30
4	Mobil Delvac 1200, SAE30	Mack Diesel 6-75	1,400	2.50	1.90
5	Texaco 30W	MBTA Diesel Bus	?	0.22	N.D.
6	Shell 30W	Mack 300, Diesel Maxidine	15,000	0.90	1.0
7	Texaco 30W	GMC 366 V-8	300	N.D.	N.D.
8	Texaco 30 W	GMC 427 V-8 diesel	38,972	Bad Sample	
9	Havoline 30W	GMC 351 V-6	2,000	*	0.54
10	Gulf 30W	? 250 L-6	4,384	*	0.40
11	Exxon 30W	GMC 366 V-8	2,584	*	N.D.
12	Texaco 30W	GMC 305 Diesel	3,484	*	0.48
13	Texaco 10 W 40	Chevrole 350 V-8 Gasoline Van	2,800	0.5	
14	Exxon SAE30 W	Ford 330 Gasoline Truck	3,000	38.8	39.2
15	Texaco 10 W 40	Pick-up Truck Gasoline	3,000	2.4	
16	Gulf 10 W 40	GMC 351 V-6 Gasoline Truck	600	3.1	3.1
17	Pennzoil SAE30	GMC 379 V-6	3,000	1.7	
18	Texaco SAE30	GMC 6V53 Detroit Diesel Truck Turbo Charged	6,000	9.2	8.4
19	Shell x-100 Multigrade	1980 Ford V-8 Gasoline Car	6,700	16.9	
20	Ford Super Premium 10 W 40	1979 Ford Mustang Gasoline Car, in line	2,460	5.2	

-continued-

Sample No.	Type of Oil	Type of Engine	Miles on Oil	DMN (ppb) GC	 HPLC
21	Wolfs Heat + Wolfs Head 20-50W + Quaker State 10 W 30 + Marvel Mystery Oil	1967 Chevrole Impala Gasoline Car, in line	121,000	7.7	6.5
23	Ford 10 W 30 Super Premium	1973 Torino Wagon V-8 Gasoline	1,000	5.6	
26	Mobil Special 10 W 30	1978 Datsun S10 Sports Coupe Gasoline, in line	4,000	9.7	9.5
28	Oilzum 10 W 40	1978 VW Diesel Car	7,991	0.7	
29	Cashol 10 W 30	Mercedes Benz 2400 Diesel Car, in line	51,803	9.2	
30	Castrol 10 W 30	BMW 320i Car	24,806	19.4	18.4
31	Castrol 6TX 20 W 50	Mercedes Benz 280 SE Gasoline Car, in line	18,282	8.1	
32	Oilzum SE 10 W 40	VW Bus 4 cylinder, opposed Gasoline	1,750	14.2	14.9
33	Conoco Super SAE30	Mercedes Benz 2400 Diesel Car, in line	51,803	9.2	

* Could not be analyzed on GC-TEA because of a co-eluting material.

Appendix G

Nitrosamine Measurements Taken During Method Development Period

Monthly Progress Report on

CRANKCASE EMISSION CHARACTERIZATION OF DIESEL ENGINES

EPA Contract 68-03-2719

11 September 1978 - 11 November 1978

Submitted by: Thermo Electron Corporation
101 First Avenue
Waltham, Mass. 02154

Written by: Ulku Goff
Approved by: David H. Fine

Introduction

This report covers the start-up of the contract. Initial attempts have been made to find an artifact free trapping system for nitrosamine analysis from crankcase emissions.

Experimental

Sampling was carried out for 30 minutes at a flow rate of about 1.65 liters per minute (L/M). This system that was used for sampling is shown in Figure 1.

Series A

4 parallel liquid traps were used. The traps contained the following collection mediums:

1. 50 ml pH:4 biphthalate buffer solution + 0.5 gm sulfamic acid + 0.5 gm L-ascorbic acid.
2. 50 ml pH:4 biphthalate buffer solution + 0.5 pm sulfamic acid + 0.5 pm L-ascorbic acid + 1 ppm morpholine.
3. 50 ml 1N NaOH solution + 0.5 gm NaN_3.
4. 50 ml 1N NaOH solution + 0.5 gm NaN_3 + 1 ppm morpholine

The liquid traps were all followed by a Thermosorb^{tm} solid absorbers. These were used so as to determine whether any Nitrosamine escaped from the liquid traps. Sulfamic acid and L-ascorbic acid were used as nitrosation (by nitrite) inhibitors. Sodium azide was used to mop up excess nitrogen oxides. Sodium azide has not been used before in Nitrosamine analysis. Morpholine was added as a check on the formation of nitrosamines under the sampling conditions. The presence of Nitroso morpholine would indicate artifact formation in the traps.

Following collection, 15 ml of the liquid trap contents were loaded onto Preptubes^{tm} and eluted with 60 ml dichloromethane (DCM) into Kuderna-Danish evaporators. The DCM was evaporated down to about 1 ml in a 55°C water bath. The sample was then analyzed on both GC and HPLC, using the TEA as the detector.

The Thermosorb tubes were eluted with 1 ml of 50/50 methanol/DCM mixture, cleaned on a silica gel column by eluting first with 5 ml pentane, then with 25 ml DCM. The DCM was evaporated in a water bath and analyzed on GC-TEA. The Thermosorb tubes could not be used without the silica gel clean up, because of oil vapors and particulate matter.

Results

All the traps contained dimethylnitrosamine (DMN) on GC-TEA, which was also confirmed on HPLC-TEA. The levels are as shown below.

1 - 0.87 μg/m^3
2 - 1.03 μg/m^3
3 - 0.83 μg/m^3
4 - 0.92 μg/m^3

The Thermosorb tubes did not have any detectable DMN, indicating that the liquid traps were retaining all the DMN. Trap 4 also contained N-nitrosomorpholine, indicating that sodium azide was not a good nitrosation inhibitor. The Nitrosomorpholine was formed during the collection.

Series B

Two parallel traps were used, containing the following:

1. 50 ml citrate-phosphate pH:4 buffer + 0.5 gm sulfamic acid + 0.5 gm L-ascorbic acid + 0.5 ml butanol-2 + 1.6 ppm diethylamine (80 μg). The length of connecting line was 6.5 ft.

2. As above with the length of the connecting line being 1 ft.

During this run different lengths of connecting tubing were used for trap 1 and 2, to check for possible artifactual formation of DMN in the transfer line.

The liquid traps were followed by Thermosorb^{tm} solid absorbers.

The contents of the liquid traps were extracted in a separatory funnel with 3 x 20 ml DCM. DCM was evaporated at 55°C in a Kuderna-Danish evaporator down to 1 ml, and then analyzed on GC-TEA.

Results

DMN levels as follows:

1 - 0.85 μg/m^3
2 - 1.1 μg/m^3

The Thermosorb washes did not contain any detectable nitrosamines. Formation of DEN was not observed.

The trap solution was checked for the presence of diethylamine (DEA) at the end of the sampling. Analysis showed the presence of 20 μg DEA in the trapping solution. This DEN was not formed, even though adequate precursor amine was still present in the trap. As a control, fresh Citrate -phosphate pH:4 buffer was analyzed for nitrosamines. No detectable background nitrosamines were found to be present in the buffer solution.

Apparatus Used

The GC analysis was made with Thermo Electron GC-661 interfaced to Thermal Energy Analyzer (TEA-502).

HPLC analysis was made using Varian 8500 pumps interfaced to TEA-502/LC. GC-column - 10% carbowax + 0.5% KOH chromasorb WHP. 80/100. Carrier gas Argon, 20 ml/min. Column temperature 125 - 150°C.

HPLC column - Lichrosorb Si60, (10 μ). Solvent - 80/10/5 isooctane/DCM/ acetone.

Bendix Mesa C-115 type air pumps were used for sample collection. The flow rate of the pumps was calibrated against a mass flowmeter (Hastings).

Summary

The formation of N-morpholine with KOH trapping system, might be occuring during the concentration step of the organic solvent. That possibility is eliminated with pH:4 buffer system, because the amines are not extracted out of the acidic solutions with organic solvent.

Future Work

Nitrosamine levels will be measured in the presence of high levels of added NO_X dimethylamine gas, and NO_X and dimethylamine present at the same time.

Measurements will also be made at different engine load and speed levels. NO_X measurements on the crankcase emissions will also be made.

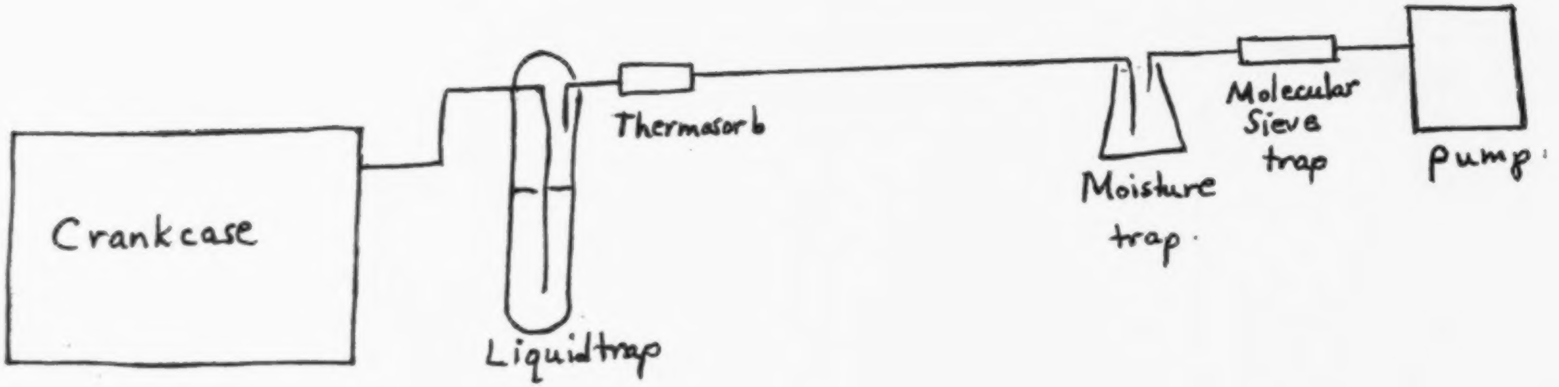

Crankcase
Liquidtrap
Thermasorb
Moisture trap
Molecular Sieve trap
pump

FIGURE 1. System for Collection of Nitrosamines from Crankcase emissions.

Monthly Progress Report on

CRANKCASE EMISSION CHARACTERIZATION OF DIESEL ENGINES

EPA Contract 68-03-2719

November 11 - December 22, 1978

Submitted by

Thermo Electron Corporation
101 First Avenue
Waltham, Mass. 02154

Written By: Ulku Goff

Approved By: David Fine

Introduction

This report covers the period between November 11 through December 22, 1978. During this period, liquid traps containing citrate-phosphate buffer and thermosorbs were examined.

Experimental

Analytical Apparatus Used

The GC analysis of liquid trap samples were made with Thermo Electron GC-661 interfaced to a Thermal Energy Analyzer (TEA-502). The GC column contained 10% Carbowax + 0.5% KOH chromosorb WHF 80/100. Carrier gas, argon, 20 ml/min, column temperature 125°C. The GC analysis of Thermosorb samples were made withShimadzu GC 6 AM interfaced to a Thermal Energy Analyzer-502. GC column contained 5% PEG Chromosorb WAW, 60/80, carrier gas argon, 50 ml/min. Temperature programming was used between 90 -120°C at a rate of 10°C/min.

Bendix Mesa C-115 type air pumps were used for sample collection. The flow rates of the pumps were calibrated against a mass flow meter (Hastings).

Engine Conditions

Light load

Oil temperature: 80°C
Blowby temperature: 49°C
Engine Speed: 1800 RPM
Load: 100 ft. lb

Medium Load

Oil temperature: 82°C
Blowby temperature: 70°C
Engine Speed: 1800 RPM
Load: 400 ft. lb.

Heavy Load

Oil temperature: 84°C

Blowby temperature: 68°C

Engine Speed: 1800 RPM

Load: 600 ft. lb.

Series C - Engine Load:High - Two parallel liquid traps contained the following collection medium:

1. 50 ml pH:4, citrate-phosphate buffer + 0.7 gm L-ascorbic acid + 0.7 gm sulfamic acid + 1 ml butanol-2 + 1.6 ppm diethylamine (80 μg).

2. 50 ml pH:4, citrate-phosphate buffer + 1.6 ppm diethylamine (DEA). In this run, a mixture of 3 ppm NO_x was bled into the system before the liquid traps. A moisture trap, consisting of a 200 ml conical flask was used before each pump.

Following the 1/2 hour collection period, the liquid trap contents were loaded on Preptubes™ and eluted with 60 ml dichloromethane (DCM) into Kuderna Danish evaporators. The DCM was evaporated down to about 1 ml in a 55°C water bath. The samples were analyzed on GC, using TEA as the detector.

Results and Conclusions

The traps contained the following amounts of dimethylnitrosamine (NDMA): 1) 1.01 $\mu g/m^3$ and 2) 1.11 $\mu g/m^3$. No diethylnitrosamine was observed indicating that the method was not susceptible to an NO_x artefact at an NO_x level of 3 ppm.

Series D - In this run, ThermoSorbs™/N Air Sampler were tried as the collection medium. They contain a solid absorber to trap nitrosamines. Two background samples were taken at the air intake point of the engine. Following a two-hour collection period, the ThermoSorbs™/N Air Sampler were eluted with 1 ml, (collected volume), 10/90 methanol/dichloromethane mixture. The samples were analyzed on GC using TEA as the detector. No detectable volatile nitrosamines were observed.

Series E - Engine Load: High

4 parallel ThermoSorbs were used. They were treated as follows:

1. Plain ThermoSorb
2. Plain ThermoSorb
3. 25 μg of morpholine was injected just before the ThermoSorb
4. 100 ppm NO + 3 ppm NO_2 was bled in just before the ThermoSorb

Following a 1 hour collection period, the ThermoSorbs were eluted with 5 ml pentane (collected volume), dried by a N_2 gas stream prior to elution with 1 ml 10/90 methanol dichloromethane mixture. The samples were analyzed on GC using TEA as the detector.

Results and Conclusions

The samples contained the following amounts of NDMA:

1. 1.0 $\mu g/m^3$
2. 1.4 $\mu g/m^3$
3. Sample was lost
4. 0.9 $\mu g/m^3$

We conclude that 100 ppm NO and 3 ppm NO_2 do not cause an artifact in the NDMA analysis.

Series F - Engine Load: Medium

Two parallel ThermoSorbs were used and treated as above.

Results

Thermosorbs contained the following amounts of NDMA:

1. 2.8 $\mu g/m^3$
2. 2.1 $\mu g/m^3$

Series G - Engine Load:Light

Two parallel Thermosorbs were used. One of the Thermosorbs could not be analyzed due to the contaminated nature of the sample.

Results and Conclusions

1. 0.6 $\mu g/m^3$.

The correlation between load, NO_x levels and nitrosamine levels will be examined.

The engine was not available between November 15 and December 18, 1978.

Summary

The samples collected on Thermosorb showed a great deal more compounds as compared to liquid traps, which might cause problems during mass spectral analysis.

Future Work

The nature of the unknown compounds will be briefly examined in order to determine whether any of them are indeed N-nitrosamines. An evaluation of liquid traps and Thermosorbs will be made. It will be decided as to which traps to use for collection of samples that are required for mass spectral analysis.

Monthly Progress Report on

CRANKCASE EMISSION CHARACTERIZATION OF DIESEL ENGINES

EPA Contract 68-03-2719

December 22, 1978 through January 22, 1979

Submitted by: New England Institute for Life Sciences
125 Second Avenue
Waltham, MA 02154

Written by: Ulku Goff
Approved by: David Fine

Introduction:

This report covers the period between December 22, 1978 through January 22, 1979

Experimental:

Analytical Apparatus Used:

The GC analyses were made with a Thermo Electron GC-661 interfaced to a TEA-502. The GC column contained 5% PEG Chromasorb WAW, 60/80. The carrier gas flow was 50 ml/min. For NDMA analyses, temperature programming from 90°C to 120°C, at a rate of 10°C/min was used. N-nitroso morpholine (NMOR) and N-nitrosopyrolidine (NPYR) analyses were carried out at a GC temperature of 170°C.

The HPLC analyses were made with a Varian 8500 LC pump interfaced to a TEA-502. The LC columns were Lichrosorb SI60 10u (3.2 mm x 250 mm) and Lichrosorb NH_2, (3.2 mm x 250 mm) and were supplied by Altex Scientific, Inc. The solvent systems were 4/17/79 Acetone/DCM/isooctane, and 10/90 DCM/isooctane respectively.

Bendix Mesa type C-115 air pumps were used for sample collection. The flow rates of the pumps were calibrated against a Hastings mass flow meter.

Samples (31-40)

Engine Conditions:

Load: 600 ft lbs

Engine speed: 1800 rpm

Oil temperature: 85°C

Blowby temperature: 63°C

Hours on the engine: 230-240

Hours on the oil: 90-100

Engine Oil: Chevron Delo 400, SAE 30

Samples (41-44)

Engine Conditions:

Load: 300-700 ft lbs

Engine Speed: 1800 rpm

Oil temperature: 83-87°C

Blowby temperature: 57-70°C

Hours on the engine: 251-255

Hours on the oil: 6-10

Engine Oil: Mobil Delvac 1200, SAE 30

Procedure:

The sampling of the crankcase exhaust was accomplished using pairs of parallel traps and the results are shown in Table I and Table II.

Following the 1 hr sampling period, the contents of the liquid traps were extracted in separatory funnel with 3 x 15ml dichloromethane (DCM). DCM was poured through 15 gms of sodium sulfate into the Kuderna-Danish (K.D.) evaporator.Sodium sulfate was washed with 5 ml of DCM. The samples were evaporated down to about 2 ml in a 55°C water bath and were analyzed by GC and HPLC, using TEA as the detector.

One ml samples of traps #41, 42 and 43 were drawn out prior to extraction and nitrosated to check for the presence of pyrolidine or any other amine that might be present in the traps. The results are given in Table III.

Results and Discussion:

The results are given in Table I and Table II. Traps #31 and 32 were spiked with 25 ug of morpholine (mor) as a check for the artifactual formation of N-MOR in the traps. These traps showed the presence of n-mor. As other traps (33-36; 39-40) were analyzed, the N-MOR levels were found to be very close to levels in traps #31 and 32. For this reason N-MOR was assumed to be present in the crankcase emissions at about 0.9 ug/m^3 level.

In traps #37 and 38, where MOR was injected into the sampling line just prior to the traps, N-MOR levels were higher. The formation of N-MOR was about 1.5% and indicating that the formation of nitrosamines was possible in the lines at 25 ug amine level.

In traps #41-44, NDMA levels were higher and the presence of N-MOR was not observed. The reason for this higher result is not clear, but the fact that the engine was operating with a fresh engine oil of a type different from previous sample runs may have had some influence, and suggests that a correlation between nitrosamine level and the age of the oil might require investigation.

In trap #43, the presence of N-PYR was not observed, indicating that the traps were artifact-free under the sampling conditions. When one ml of the above trap solution was nitrosated, N-PYR was formed indicating that, at the end of sampling, pyrolidine was still remaining in the traps, available for nitrosation.

In Table III, nitrosated samples show the presence of DMA and MOR, indicating that the nitrosamine precursors were present in the crankcase emissions. Engine fuel or the oil itself might be the source of the possible nitrosamine contamination. A preliminary analysis of engine fuel by GC-TEA showed the presence of 18 ppb NDMA concentration.

The analytical results of samples collected on Thermosorb™ tubes were not conclusive due to contamination of the nitrosamines with co-eluting materials. Since a clean-up procedure would mean extended analysis time and lowered recoveries, the liquid traps were preferred for the analysis.

None of the above results were corrected for recoveries.

Combined samples (traps 33, 34, 35, 36, 39, 40) and sample #44 were sent for mass-spectral analysis.

Conclusion:

The engine crankcase emission contained NDMA at levels varying from 3.1 ug/m^3 (average) to 11.9 ug/m^3 (average) and N-MOR from non-detectable to 0.9 ug/m^3 (average) depending on oil. Mass-spectrometric confirmation is underway.

Expenditures:

As of January 14, 1979, $25,144 was spent, bringing the balance to $67,449.

Table I. Nitrosamine levels in crankcase emissions, using engine oil: Chevron Delo 400, SAE 30.

Trap #	Solution	NDMA (ug/m^3)	N-MOR (ug/m^3)
31	40 ml, PH:4 Citrate-Phos Buffer + 25 ug morp.	3.1	1.1
32	40 ml, PH:4 Citrate-Phos Buffer + 25 ug morp. + 1 ml Butanol-2 + 0.5 gm Ascorbic A.	3.0	1.2
33	40 ml, PH:4 Citrate-Phos Buffer + 1 ml Butanol-2 + 0.5 gm Ascorbic A.	3.1	0.4
34	40 ml, PH:4 Citrate-Phos Buffer	2.8	0.9
35	40 ml, PH:4 Citrate-Phos Buffer	2.6	0.7
36	40 ml, PH:4 Citrate-Phos Buffer	2.8	1.1
37	40 ml, PH:4 Citrate-Phos Buffer + 25 ug morpholine injected into the line + 0.5 gm Ascorbic A + 1 ml Butanol	3.5	6.4
38	40 ml, PH:4 Citrate-Phos Buffer + 25 ug morpholine injected into the line	3.3	5.2
39	40 ml, PH:4 Citrate-Phos. Buffer + 1 ml Butanol-2 + 0.5 gm Ascorbic A	3.4	0.9
40	40 ml, PH:4 Citrte-Phos. Buffer	3.5	1.1

Table II. Nitrosamine levels in crankcase emissions, using engine oil:

Mobil Delvac 1200, SAE 30

Trap	Solution	NDMA ($\mu g/m^3$) G.C.	NDMA ($\mu g/m^3$) HPLC	N-MOR ($\mu g/m^3$)	N-PYR ($\mu g/m^3$)
41	40 µl, pH: 4 citrate-phos buffer	12.6	11.5	N D	
42	40 µl, pH: 4 citrate-phos buffer	11.4	10.0	N D	
43	40 µl, pH: 4 citrate-phos buffer + 50 µg pyrolidine	11.1	11.3	N D	N D
44	40 µl, pH:4 citrate-phos buffer	12.5	11.9	N D	

Table III. Trap Contents that had been nitrosated

Trap	NDMA	DMA (after nitrosation)	N-MOR	MOR (after nitrosation)	N-PYR (after nitrosation)
41	12.6 µg/m^3	44 ng/ml	ND		ND
42	11.4 µg/m^3	76 ng/ml	ND	11.5 ng/ml	ND
43	11.1 µg/m^3	53 ng/ml	ND	11.0 ng/ml	122 ng/ml (spike)

Monthly Progress Report on

CRANKCASE EMISSION CHARACTERIZATION OF DIESEL ENGINES

EPA Contract 68-03-2719

January 22, 1979 through February 22, 1979

Submitted by: New England Institute for Life Sciences
125 Second Avenue
Waltham, Mass. 02154

Written by: Ulku Goff
Approved by: David H. Fine

Introduction:

This report covers the period between January 22 through February 22, 1979. During this period, some artifact and blank experiments were carried out in relation to crankcase emission analysis. Confirmatory tests were performed on NDMA found in emissions.

A method was developed for oil analysis and 11 oil samples were analyzed on GC-TEA and HPLC-TEA.

Experimental:

Analytical Apparatus Used:

The GC analyses were made with a Thermo Electron GC-661 interfaced to TEA-502. The GC columns contained 5% PEG Chromasorb WAW, 60/80 and 10% Carbowax 20M + 0.5% KOH on Chromosorb WHP, 80/100. NDMA analyses were carried out at 120°C, N-pyr and N-MOR analyses were carried at 170°C.

The HPLC analyses were made with Varian 8500 LC pump interfaced to a TEA-502. The LC columns were μPorasil 10μ (3.9 mm x 300 mm) and Lichrosorb Si60, 10μ (3.2 mm x 250 mm). The solvent systems were 5/95 acetone-isooctane and 7/93 acetone/isooctane respectively.

Crankcase Emission Samples (45-46)

Engines Conditions:

Load: 160-600 ft lbs

Engine speed: 1800 rpm

Oil temperature: 82-88°C

Blowby temperature: 69-71°C

Hours on the engine: 268

Hours on the oil: 23

Engine oil: Mobil Delvac 1200, SAE 30

Procedure:

The sampling and analysis of crankcase exhaust was done as explained in the previous report, but the sampling period was reduced to 1/2 hour. The results are given in Table 1.

One ml samples of the traps #45 and 46 were drawn out prior to extraction and nitrosated to check for the presence of amines. The results are given in Table II.

pH:4 citrate-phosphate buffer blank and pH:4 buffer + NO_x blank experiments were carried out according to the procedures below:

pH:4 citrate-phosphate buffer blank experiment:

40 ml of the buffer solution was kept at 35°C (temperature above engine) in water bath and air was pulled through it for 1 hour. Trap contents were treated as the real samples.

pH:4 citrate-phosphate buffer + NO_x blank experiment:

40 ml of the buffer solution was kept in 35°C water bath. While 2.2 l / min air was pulled through the buffer solution, 109 ppm NO + 7.7 ppm NO_2 were bled in for 1 hour. Trap contents were analyzed as the real samples.

Confirmatory Tests:

Samples #45 and 46 were combined and cleaned on aluminum oxide (II-III). The presence of NDMA was confirmed by the following tests.

1) HPLC
2) The combined sample was spiked with NDEA and irradiated with UV for 1 hour and analyzed on GC-TEA

3) The combined sample was spiked with NDEA and treated with glacial acetic acid for 1 hour and analyzed on GC-TEA.

Oil and Fuel Analysis:

#2 fuel oil was obtained from the fuel tank of Mack diesel 675. 30 ml of the fuel was spiked with NDEA at 95.3 ppb level and extracted with 2 x 5 ml 25% MeoH in H_2O in a separatory funnel. MeoH/H_2O layer was poured into a Preptube and extracted with 50 ml DCM. DCM was reduced to 1 ml in 55°C water bath. The results are given in Table III and IV. Oil samples were obtained from local auto dealers and service stations and were analyzed by bubbling air for 1 hour through a 50 ml oil sample which had been heated to 110°C. 0.5 gm ascorbic acid, dissolved in 1 ml water and 3 drops of α-tocopherol were added into oil as nitrosation inhibitors (Fig. I). Nitrosamines were collected on Thermosorb tubes and were eluted with 1 ml Methanol. The Thermosorb tubes and oil were shown to be artifact free by spiking with an amine and looking for the formation of corresponding nitrosamines. The air used, was checked for the presence of nitrosating agents by placing a morpholine spiked Thermosorb at the air inlet of the flask. There was no formation of N-MOR. The results of the oil analyses are given in Tables III and IV.

Nitrosation of Mobil Delvac 1200, SAE30:

A 50 ml sample of the above metioned oil was placed in a 500 ml flask and a mixture of air + NO_x (100 ppm NO + 7 ppm NO_2) was bubbled through the oil at 110°C for 1 hour. Nitrosamines were collected on Thermosorb and eluted with 1 ml Methanol. The results are given in Table III.

Results and Discussion:

In trap #46, the presence of N-pyr was not observed. This indicates that the traps were artifact free even at high NO_x levels. The agreement of the NDMA levels in both traps indicates the same thing.

When trap contents were nitrosated, they showed the presence of N-pyr indicating that pyr was remaining in the traps, available for nitrosation during the sampling. Formation of high quantities of NDMA indicated the presence of DMA in the crankcase emissions. The blank experiments showed no detectable amounts of nitrosamines with or without the presence of NO_x.

The complete destruction of the NDMA-TEA signal by UV irradiation and no change of signal with treatment by glacial acetic acid points to a pure NDMA signal.

Conclusion:

Amounts of NDMA in the oil samples varied from non-detectable levels to 2.5 ppb. When a sample of Mobil Delvac 1200, SAE30 was nitrosated by NO_x, the NDMA level was raised to 11.5 ppb indicating that the nitrosatable precursers of NDMA exist in the oil sample and can be nitrosated by NO_x. So it appears, then, that the oil used is a very likely source of nitrosamines in the emissions.

Table 1
Nitrosamine Levels in Crankcase Emissions, Using Engine Oil:
Mobil Delvac 1200 SAE30

Trap No.	Solution	NDMA ($\mu g/m^3$)	N-pyr (ng/ml)
45	40 ml, pH:4 Citrate-phosphate Buffer + 62.8 μg pyrrolidine	8.4	N.D.
46	40 ml, pH:4 Citrate-phosphate Buffer + 62.8 μg pyrrolidine + 215 ppm NO + 15.3 ppm NO_2	9.0	N.D.

TABLE II. Trap Contents that had been Nitrosated

Trap #	DMA	PYR
45	14.5 ng/ml	182.5 ng/ml (spike)
46	40.0 ng/ml	254.1 ng/ml (spike)

TABLE III. Oil and Fuel Analysis

	Type of Oil	Type of Engine	Miles on the Oil	DMN (ppb) GC	DMN (ppb) HPLC	DMN after Nitrosation
1.	Gulf 30W	Detroit Diesel 6-71	7000	0.60	0.60	
2.	Gulf 30W	Detroit Diesel 6-71	8975	0.95	0.70	
3.	Chevron Delo 400, SAE30	Mack Diesel 6-76	6000	1.50	1.30	
4.	Mobil Delvac 1200, SAE30	Mack Diesel 6-75	1400	2.50	1.90	11.5
5.	Texaco 30W	MBTA Diesel Bus	?	0.22	N.D.	
6.	Shell 30W	Mack 300, Diesel Maxidine	15,000	0.90	1.0	
7.	Texaco 30W	GMC 366 V-8	300	N.D.	N.D.	
8.	Texaco 30W	GMC 427 V-8 Diesel	38,972	- Bad Sample -		
9.	Havoline 30W	GMC 351 V-6	2000	*	0.54	
10.	Gulf 30W	? 250 L-6	4384	*	0.40	
11.	Exxon 30W	GMC 366 V-8	2584	*	N.D.	
12.	Texaco 30W	GMC 305 Diesel	3484	*	0.48	
13.	#2 Fuel Oil			9.0	3.0	

* Could not be analyzed on GC-TEA, because of a co-eluting material

TABLE IV. Oil and Fuel Nitrosamine Recoveries and Detection Limits

Oils		Recoveries (%)	Detection Limit (ppb)
	DMN	80	0.1
	DEN	73	0.2
	DPN	40	0.7
	DBN	7	2.5
	N-pip	23	0.8
	N-pyr	29	0.8
	N-Mor	29	0.8
Fuel Oil	DEN	75	0.5

Appendix H

Diesel Tailpipe Exhaust Analysis for Nitrosamines

While at SWRI, we ran three tests on Mack Diesel exhaust using pH4 phosphate-citrate buffer traps as the collection medium. The extraction of nitrosamines from the traps were carried out as described in Section III, TASK I. The results are described below.

Fuel: National Average #2 (Sulfur Content: 0.235% by weight).

Engine: Mack ETAY (B) 673A

Mode	Oil	NDMA ($\mu g/m^3$)	NDMA ($\mu g/min$)
5	Amoco 300 SAE30	0.8	13.4
3 - 4	Mobil Delvac Super 15 W 40	0.3	N.D.
2	Mobil Delvac Super 15 W 40	1.1	13.8

N.D. - Not Determined

Appendix I

Nitrogen Content of Some of the Oils

Type of Oil	Nitrogen Content %	Nitrosated (ppb) NDMA	Nitrosated (ppb) NMOR
Arco fleet plus S-3 15 W 40	0.1	2.0	3.3
Arco fleet plus S-3 30 W	0.1	4.8	N.D.
Chevron Delo 400 15 W 40	0.2	5.4	N.D.
Chevron Delo 400 30 W	0.17	N.D.	N.D.
Chevron Delo 300 30 W	0.01	1.0	N.D.
Chevron Delo 100 30 W	0.03	0.5	N.D.
Exxon HD X Plus 30 W	0.08	1.0	N.D.
Exxon HD-3	0.1		N.D.
Exxon HD-3	0.11		N.D.
Gulf Super Duty Motor Oil 30 W	0.048	1.3	N.D.
Gulf Lub Motor Oil XHD 30 W	0.013	0.8	N.D.
Gulf Super Duty Motor Oil 15 W 40	0.056	1.3	N.D.
Gulf Lub Motor Oil XHD 10 W 30	0.013		
Gulf Lub XHD 30 W	0.013	0.7	N.D.
Mobil Delvac 1200 30 W	0.04	15.0	7.7
Mobil Delvac Super 15 W 40	0.05	39.0	1.0
Shell Rotella 15 W 40	0.13	1.0	1.4
Shell Rotella 30 W	0.13	2.4	5.6
Valvoline HD Super HPD 30 W	0.025	N.D.	N.D.
Valvoline All-fleet 30 W	0.02	1.6	N.D.
Valvoline All-fleet 15 W 40	0.022	0.8	N.D.

*$r = -0.06$
*$r^2 = 3.7 \times 10^{-3}$

*Excluding the Mobil Data:
*$r = 0.51$
*$r^2 = 0.26$

*r (correlation coefficient), was obtained from the least-squares linear regression analysis of the two variables, namely, nitrogen content of the oil and NDMA content of the nitrosated oil.

Appendix J

Background on Nitrosamines

BACKGROUND ON NITROSAMINES

I. INTRODUCTION

The interest in N-nitroso compounds (N-nitrosamines) began following the observation in animals of the toxic and carcinogenic effects of N-nitrosodimethylamine (NDMA) (Barnes, J.M. and Magee, P.N., 1954; Magee, P.N. and Barnes, J.M., 1956).

The first report of their toxic effect on humans was a report by Freund, H.A. (1937) who described the hepatotoxic effect of NDMA after autopsy findings of two chemists indicated that they have been accidentally poisoned by this compound. Since these findings, several N-nitroso compounds have been extensively investigated for their carcinogenicity by Druckrey et al (1967) and reviewed by Magee and Barnes (1967). More recent reviews of their toxicity (Magee, P.N.; Swann, P.F., 1969), carcinogenicity and metabolism (Magee, P.N. et al, 1976), and mutagenicity (Montesano, R. and Bartsch, H., 1976; Neale, S., 1976) are also available. What these studies have demonstrated are that many of these compounds are potent carcinogens that have a high degree of specificity in inducing tumors in various species and among target organs within the same species. Over 100 of the approximately 130 different N-nitroso compounds tested proved to be carcinogenic in these studies and in a variety of animal species. For example, N-nitrosodiethylamine (NDEA) has been tested in at least 14 different animal species and none were found dependent upon the structure of the N-nitroso compound and the route of administration in the test animal. Dose response studies using NDMA and NDEA with less than 100 rats have indicated that doses as low as 1-5 ppm of these compounds in the diets are marginally carcinogenic. While many of these N-nitroso compounds have been demonstrated to be potent animal carcinogens, their carcinogenic risk to man (the probability that defined exposures to these chemicals will lead to or increase incidence of cancer in man) has not yet been assessed.

In order to address the topic of the possible carcinogenic hazard that N-nitroso compounds may pose for humans, it is necessary to locate sufficient populations of exposed people to determine these effects. However, until such epidemiological assessments can be made, it must be assumed, on the basis of the many animal studies, that humans will not be uniquely resistant to their carcinogenic action. Indeed if human populations are found that have excessive (higher than justifiable) exposure to these compound, prompt action should be taken to eliminate or reduce their exposure. Since cancer produced from carcinogenic compounds is a delayed toxic effect and since animal studies show dose related responses to these agents it would be prudent to assume (until evidence can be obtained) that any exposure to the carcinogenic N-nitrosamines constitute a risk.

Until as recently as 1975 most of the interest in the environmental occurrence of N-nitroso compounds centered around their occurrence in nitrite preserved foods such as cheese products, fish, and fish meal and biological samples and in *in vivo* formation from precursor chemicals. With the discovery of NDMA in the atmosphere of an urban area in Baltimore, Maryland (Fine, D.H. et al, 1976), near a facility manufacuring 1,1-dimethylhydrazine (a rocket fuel) from NDMA and in the air near a large producer of dimethylamine in Charlestown, West Virginia, the environmental emphasis on these compounds began to shift. Further discoveries of N-nitroso compounds in products and environments such as cosmetics (Fan, T.Y. et al, 1977a), tobacco and tobacco smoke (Hofmann, D., et al

1974; Singer, S.S. et al, 1978; Fan, T.Y. et al, 1978).

In view of the many possible synthetic pathways for the formation of N-nitrosamines, human exposure to these compounds is a virtual certainty. Such exposure is most likely to occur if the precursors exist together in materials having human contact (e.g. foods, air, drugs, cosmetics, drinking water, etc.) or if such materials already contain pre-formed nitrosamines. In fact, the list of items that have now been demonstrated to contain measurable levels of preformed N-nitroso compounds has grown considerably over the past decade. Many secondary amines such as dimethylamine, diethylamine and morpholine are produced in large quantities for industrial and consumer use. Products produced from these amines are, for example, used in agricultural chemicals, detergents, rust inhibitors, rubber additives, solvents, drugs, plastics, leather tanning, textiles, cosmetics, synthetic cutting and grinding fluids, etc (Mitre Technical Report, 1976). Of particular interest to this work is the fact that many of the oil additives that are commonly used in crankcase oils contain amines or amine generating compounds. Given the wide spread use of amines and the ubiquitous presence of nitrous oxides both in the air and, especially, in crankcase atmospheres, the likelihood of N-nitrosamines being found in these products is high.

II. CHEMISTRY

The preparation of N-nitroso compounds in the laboratory has traditionally involved the reaction between a secondary amine and sodium nitrite under acidic conditions (Boyer, J.H., 1969; Fridman, A.L. et al, 1971). This amine nitrosation reaction has been studied in considerable detail by a number of investigators, and has been extended to include reactions with various amine derivatives such as amides, ureas, guanidines, carbamates, peptides, nucleosides, lactams, etc. The kinetics and mechanism of the reaction with nitrite under acidic conditions has been discussed (Fridman, A.L. et al, 1971; Mirvish, S.S., 1977). Not only can secondary amines undergo nitrosation by nitrite, but it has long been known that tertiary amines can also partake in this reaction (Fridman, A.L. et al, 1971). Most recently, Tannenbaum et al (1978) have demonstrated the formation of N-nitrosamines from primary amines and nitrite, as well as catalytic effects by inorganic thiocyanate. The overall yields for these types of reactions, in the absence of a catalyst, are generally low (0.1-0.5%). A general review of the reactions of primary amines with nitrous acid is available (Scanlan, R.A., 1975), and possible reaction pathways have been proposed (Wartheson, J.J. et al, 1975).

N-nitrosation reactions are generally slow at neutral or alkaline pH due to low equilibrium concentration of the active nitrosating intermediate, nitrous anhydride (N_2O_3). However, an appreciable nitrosation rate for secondary amines can occur at pH 6-11 in the presence of suitable catalysts such as chloral or formaldehyde (Roller, P.P. and Keefer, L.K., 1974). Keefer has also shown that various metal ions can catalyze these reactions under basic conditions (Keefer, L.K., 1976). N-nitrosamine formation has also been shown to be accelerated by certain micro-organisms at acidic pH (Archer, M.C. et al, 1978). Still other catalysts have been recently elucidated with regard to the basic nitrous acid reaction (Davies, R. et al, 1978). Inhibition of the nitrous acid nitrosation reaction has been shown with a wide variety of inorganic and organic compounds, such as ascorbic acid, sulfamic acid, tocopherol, and others (Fan, T.Y. et al, 1977; Mirvish, S.S., 1975; Groenen, P.J., 1977; Mergens, W.J.

et al, 1978: Archer, M.C. et al, 1975; Douglass, M.L. et al, 1978).

Tertiary amine type compounds also undergo the nitrosation reaction with nitrous acid, and this subject has been extensively reviewed (Boyer, J.H., 1969; Mirvish, S.S., 1975; Hein, G.E., 1963). Although most tertiary amines possess low rates of nitrosation under the usual reaction conditions, examples have been shown to undergo a rather rapid formation of N-nitrosamines (Lijinsky, W. et al, 1973; Eisenbrand, G. et al, 1979). A detailed study of the mechanisms of nitrosation of tertiary amines by nitrous acid has recently been presented by Ohshima and Kawabata (1978). They also discuss the formation of N-nitrosamines from two tertiary amine oxides.

For many years, it was assumed that the most important system for nitrosation of amines was nitrous acid (or nitrous anhydride, N_2O_3). It is now apparent that several other routes are available for the efficient conversion of amines to their N-nitroso derivatives. Thus, Challis and Kyrtopoulos have demonstrated that under oxygen rich conditions, nitric oxide itself can nitrosate both primary and secondary amines in organic solvents (Challis, B.C. et al, 1978). However, under these conditions, nitric oxide itself is a poor nitrosating agent, and presumably it is the oxidation product, nitrogen dioxide and subsequent products, that are the effective nitrosating agents. Challis et al, have also demonstrated a catalytic effect on the reaction with nitric oxides by inorganic metal salts and molecular iodine (Challis, B.C. et al, 1978). Some of the salts effective in these reactions were those of zinc, copper, iron, and silver, but the most effective catalyst was I_2. These metal salts catalyzed reactions in organic solvents are considerably faster in the rate of N-nitrosamine formation than comparable reactions with nitrous acid.

It has been known for many years that certain oxides of nitrogen, viz., N_2O_3 (nitrous anhydride) and N_2O_4 (dinitrogen tetroxide) can readily nitrosate amines and amine derivatives (Fridman, A.L. et al, 1971; Challis, B.C. et al, 1978). However, it has only been recently demonstrated that both primary and secondary amines react in neutral and alkaline aqueous media (pH 7-14) to form the corresponding N-nitrosamines (Challis, B.C. et al, 1978). The mechanism of nitrosation by complex nitrogen oxides have been discussed by Challis and Kyrtopoulos (1979).

Another route for the formation of N-nitrosamines involves a reaction termed transnitrosation, whereby the nitrosyl group of a N-nitrosamine may be transferred to a secondary amine. Thus, in the case of N-nitrosodiphenylamine and morpholine, under the appropriate solvent and temperature conditions, it is possible to generate N-nitrosomorpholine and diphenylamine. Transnitrosation involving N-nitrosamines have been extensively studied by Buglass et al (1974) and more recently by Singer et al (1978). Transnitrosation by aromatic N-nitroso derivatives appears to be rapid under elevated thermal conditions in nonpolar, organic solvents, polar solvents, and under aqueous acidic conditions. It is possible that transnitrosation can also occur from other nitrosyl donor compounds, such as C-nitroso, S-nitroso, etc. The nitrosation reactions by organic nitrite (O-NO) have been known for some time, and constitute one of the established methods for the preparation of N-nitrosamines (Boyer, J.H., 1969; Fridman, A.L., 1971). This may be considered a transnitrosation reaction, since it involves the transfer of the nitrosyl group from a donor molecule (O-NO) to an acceptor molecule, the secondary amine. The mechanism of nitrosation by organic nitrites (-O-NO) may also involve the intermediacy of nitric oxide, which is then oxidized to nitrogen dioxide. Thus, the mechanism may involve the intermediate dinitrogen tetraxide (N_2O_4) as the active nitrosating species (Challis, B.C. et al, 1978).

Nitrosation of amines by aliphatic C-nitro compounds has been known for the past fifty years (Fridman, A.L. et al, 1971). Tetranitromethane for example effectively nitrosates amines to form the corresponding N-nitrosamines. This type of reaction has recently been studied in greater depth by Fan, T.Y. et al, both with regard to the generality of the reaction and its application to other amines. It would seem that many aliphatic C-nitro and aromatic C-nitro compounds can nitrosate secondary amines, as well as tertiary amines, to varying extents.

From a synthetic point of view, there are many other methods for the preparation of N-nitrosamines in the laboratory. They may involve the use of nitrosyl halides, nitrosonium tetrafluoroborate, and other nitrosyl donor reagents (Boyer, J.H, 1969; Fridman, A.L. et al, 1971). However, in general, these methods for the formation of N-nitrosamines are not as widely employed as those previously mentioned.

III. ANALYTICAL METHODS

In order to successfully determine the extent of N-nitrosamines in the crankcase emissions at the part-per-billion ($\mu g/m^3$) or the part-per-trillion (ng/m^3) level, it is essential to have analytical techniques that are sensitive, selective and free of false results. Without a sensitive and selective detection method, screening for N-nitroso compounds would be both costly and time consuming.

The analtyical system used in this study employed both gas chromatography and high pressure liquid chromatography with detection by a TEA analyzer (Krull, I.S. et al, 1978). The TEA analyzer is specifically designed for the detection of N-nitroso compounds at the part-per-trillion (ppt) level. False positive or false negative findings of N-nitroso compounds, can arise from either the creation or loss of these compounds due to the analytical method employed in sampling, sample preparation or detection. This problem of false results can arise in analytical determination of any compound. However, in the case of N-nitroso compounds the problem of false results is further aggravated by the multitude of reactant and reaction conditions that can give rise to these compounds (Krull, I.S. et al, 1978). Furthermore, some of these compounds are relatively unstable and/or volatile and losses during the sample work-up or analysis can result.

In choosing the methods for screening crankcase emissions for N-nitrosamines we were mindful of those factors that may adversely effect the analysis. N-nitrosamines are relatively easy to make and are also fairly labile. They are sensitive to prolonged thermal treatment, as well as photochemical degradation (Polo, J. and Chow, Y.L., 1976; Doerr, R.C. and Fiddler, W., 1977). In addition, certain N-nitroso derivatives are not stable to excessive conditions of pH, and beta-hydroxynitrosamines undergo degradation under alkaline conditions (Loeppky, R.N. and Christiansen, R., 1978). Most, if not all, N-nitroso derivatives undergo reactions with inorganic acids, and this has formed the basis for the denitrosation of such compounds (Downes, M.Y. et al, 1976). The acids active in denitrosation of N-nitrosamines are halogen acids, such as HCl, HBr, and HI (Eizember, R.F. et al, 1978). With regard to photochemical reactivity, Fiddler, et al (1978) have shown that most volatile N-nitrosamines, and presumably nonvolatile ones also, are rapidly destroyed by the action of ultraviolet light.

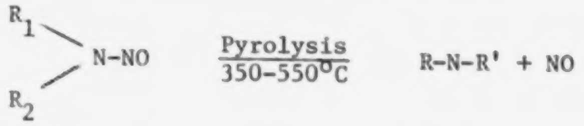
One of the most significant physical properties of N-nitroso derivatives is the relative ease of dissociation of the N-NO bond. For example, in N-nitrosodiphenylamine, the energy required to break the C-N bond is 105 kcal/mole, whereas the bond dissociation energy for the N-NO bond is only 11 kcal/mole. For simple dialkylnitrosamines, the energy required for the N-NO bond dissociation is on the order of 40-60 kcal/mole. This relatively low energy requirement for release of nitric oxide from N-nitrosamines means that exposure of N-nitroso compounds to temperatures of (400-500°C), can be a selective method for the removal of nitric oxide. It is this physical property of N-nitrosamines that allowed for the successful development of the TEA™ analyzer (Krull, I.S. et al, 1978).

TEA™ ANALYZER

In 1973, Fine and Rufeh proposed the use of chemiluminescence to detect N-nitrosamines via the formation of the nitrosyl radical, after thermal cleavage of the N-NO bond (Fine, D.H and Rufeh, F., 1974). This system has been successfully developed by Fine et al (1975). A gas chromatograph, operated isothermally or with temperature programming, can be interfaced to the TEA analyzer (Fine, D.H. and Rounbehler, D.P., 1976; Castegnaro, M. and Walker, E.A., 1978; Havery, D.C. et al, 1978).

GAS CHROMATOGRAPHY - TEA™ ANALYZER

This system operates by having gaseous samples exiting the GC swept through a catalytic pyrolyzer by the GC carrier gas, usually argon. All N-nitroso compounds present in the sample entering the pyrolyzer are cleaved at the N-NO bond, thereby releasing the nitrosyl racical (NO). The yield of NO is approximately stoichiometric for most N-nitrosamnes. Solvent vapor, pyrolysis products, and NO pass through a cold trap at -150°C which, in principle, removes all materials other than the permanent gases. The NO and the carrier gas are then swept into a low-pressure reaction chamber, where the NO reacts with ozone to generate electronically excited singlet state nitrogen dioxide (NO_2*). The key reactions occurring in the reaction chamber are:



$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + \text{light}$$

The excited NO_2* then decays back to its ground state with the concomitant emission of light near the infra-red region of the spectrum (0.6 - 2.8μ). The intensity of the light emitted is a direct measure of the amount of N-nitroso compound present in the sample. The TEA analyzer system is selective because it produces a response only if a compound meets several requirements. Thus, pyrolysis must occur within a few seconds within the catalytic pyrolysis tube at a moderate temperature, to give a product which survives a cold trap, and reactions with ozone at reduced pressure. The product of this reaction must then emit light in the near infra-red region of the spectrum. The chemiluminescent reactions must be sufficiently rapid for the emission to occur before the reactants leave the reaction chamber. Because of the relative selectivty of the TEA analyzer, it is possible to analyze N-nitroso compounds quantitatively at high sensitivity, even in the presence of many co-eluting compounds. This reduces the clean-up procedures for samples prior to the GC-TEA step. The detection limit in GC-TEA is routinely less than 100 pg (10^{-12}g) for NDMA or NPYR.

It should be mentioned that the TEA analyzer is not totally specific for N-nitrosamines alone (Stephany, R. and Schuller, P.L., 1977; Lafleur, A. et al, 1978). Thus, several other classes of organic compounds will also respond to the TEA analyzer, to varying molar extents, depending on the structure of such compounds. Organic nitrites (O-NO), N-nitrosamines ($N-NO_2$), C-nitroso (C-NO), poly C-nitro ($C-NO_2$), nitrates ($O-NO_2$) and inorganic nitrite may produce responses to the TEA analyzer. It is also probable that other classes of organic compounds, e.g., S-nitroso and S-nitro will also be found to respond on the TEA analyzer. Thus, the presence of a response by GC-TEA for a new sample can not necessarily be taken as proof of the presence of an N-nitroso compound. Confirmation of positive results is necessary, either by the use of chemical tests and/or by the use of high resolution mass spectrometry. There is strong evidence that high resolution mass spectrometry with continuous peak matching is a reliable confirmatory technique for the identification of N-nitrosamines (Gough, T.A. et al, 1977).

Various applications of GC-TEA for the determination of volatile N-nitrosamines have been reported in the literature. Collaborative studies conducted by the International Agency for Research on Cancer (IARC) employing widely differing analytical methods in different laboratories have been reported (Castegnaro, M. and Walker, E.A., 1978; Havery, D.C. et al, 1978). Both qualitatively and quantitatively, there was good agreement with the "correct" (spiked) value by both GC-TEA and high resolution mass spectrometry with continuous peak matching. The TEA analyzer has two major advantages over other detectors for N-nitroso compounds. It is generally up to 100 times more sensitive than alternative, routine GC detectors such as mass spectrometry and flame ionization or alkali flame ionization types. Also, the TEA analyzer is more selective for the N-nitroso moiety than other detectors. This selectivity, with the reservations already mentioned, allows the TEA analyzer to be used as maximum sensitivity, even for the most complex and crude samples. Such a feature allows for only minimal sample clean-up and pre-concentration prior to analysis. This greatly reduces the possibility for artifact formation and/or loss.

GAS CHROMATOGRAPHY - MASS SPECTROMETRY

Mass Spectrometry (MS) combined with gas chromatography has customarily been used for the analyis of GC amenable N-nitrosamines. The spectral fragmentation patterns of many N-nitrosamines have been documented, and several papers detail the fragmentation pathways for a number of N-nitroso compounds (Gough, T.A. and Webb, K.S., 1973; Dooley, C.J. et al, 1973). Gadbois, D.F. et al (1975) and Gaffield, W. et al (1976) have presented information on chemical ionization mass spectrometry. Mass spectrometric techniques for the analysis of volatile N-nitrosamines have been reviewed recently by Gough, T.A. (1978).

It has been observed by Gough and Webb (1973) and Dooley et al (1973, that even with high resolution, a potentially interfering fragment ($^{29}Si(Me)_3$) with a retention time close to that of NDMA may be encountered. A resolution of 70,000 is required for complete separation, and a mismatch between the two compounds can be observed even at a resolution of 7,000. Other potentially undesirable effects have been observed by Gough et al (1977) and may arise from the method of displaying the high resolution signal. Under certain conditions, co-eluted materials on the GC may suppress the mass spectrometer response and hence effect quantitation (Stephany, R.W., 1977). This, and other problems, can be overcome by the use of a peak matching technique. Here, the mass region in the vicinity of the reference fragment (usually derived from a fluorinated hydrocarbon) and the N-nitrosamine fragment of the same approximate mass are alternatively scanned every few seconds. The method allows for the observance of the reference peak as well as the rise and fall of the N-nitrosamine peak. Monitoring only the precise mass of the parent N-nitrosamine ion using high resolution mass spectrometry can lead to erroneous results (Gough, T.A. et al, 1977). One of the most reliable procedures for identifying N-nitrosamines is by mass spectrometry, using selective ion monitoring and continuous peak matching with high resolution, after initial GC separation (Gough, T.A. et al, 1977; Gough T.A., 1978). Low resolution mass spectrometers are less costly and more widely available, and they can be used successfully on relatively clean extracts, particularly for compounds having long GC retention times and complex fragmentation patterns. It should be noted that parent ion monitoring at high resolution with peak matching requires considerable operator skill. Also, not all commercially available multi-ion monitoring units are suitable for use at high resolution, and they cannot normally be used with a wide mass range without a loss of sensitivity at the higher mass region.

HIGH PRESSURE LIQUID CHROMATOGRAPHY - TEA™ ANALYZER

The TEA analyzer, when operated in the HPLC mode operates on the same basic principles ar discussed above with regard to GC-TEA. However, here a liquid sample is swept through the catalytical pyrolyzer by argon carrier gas, and all organic materials are quickly vaporized and/or pyrolyzed. Following the pyrolyzer, the solvents are condensed out inside large (300 ml) vacuum cold traps, prior to entering the chemiluminescent chamber.

At the low temperatures used in the cold traps, only the carrier gas, the nitrosyl radical (NO), and a very few, low molecular weight organic species pass through both cold traps. The remaining TEA operations are identical to those already described for the GC-TEA mode.

With the HPLC-TEA, screening procedures for background N-nitroso compounds can proceed relatively rapidly, and a large number of samples can be studied in a short period of time. Exhaustive extraction of environmental or industrial products, followed by HPLC-TEA determinations, allows for the rapid establishment of upper limits of background N-nitroso compound levels. With HPLC-TEA, the limits of detection for most N-nitrosamines are in the range of 0.1 - 1.0 ng, per injection. This allows for a sensitivity range of approximately 10-100 ppb for most compounds, but this depends upon the particular sample preparation and chromatographic conditions employed in any given analysis.

IV. ARTIFACTS (false positive and negative results)

The problem with false negatives are more managable and less of a concern than is the problem of false positives. False negatives can arise from loss of sample from the traps during collection, sample exposure to UV or sunlight, or by acid degradation of the collected N-nitrosamines. Internal analytical controls using an added known N-nitrosamine will reveal any tendacy of the chosen analytical method to degrade the N-nitrosamines. As yet there is no evidence that indicates the false negatives are a major problem with the analytical methods used in this study. A large number of laboratory and field studies have demonstrated that airborne nitrosamines are completely trapped in our system. Photo degradation is minimized by either protecting the sample by light exclusion or by avoiding strong light sources when the samples are taken.

A major source of false positives are either cross contamination or artifact formation of N-nitrosamines during the trapping or sample work-up steps. Another problem lies in the area of TEA detected unknown compounds, i.e., compounds for which we have no standards that match the observed chromatographic elution time. This problem of artifacts in the analysis for N-nitrosamines has been reviewed recently by Krull, I.S. et al (1978) and control of contamination has been extensively discussed by Zief, M. and Mitchell, J.W. (1976).

Because the detection techniques used in this study are highly specific for only those compounds which can release the nitrosyl moiety, the overall problem of contamination is limited to those compounds. However, when performing routine analysis in the ppm-ppb range, the problem of contamination is still relevant. To control for contamination, negative blanks are regularly used. These blanks include every step used in the analysis, including the same batches of chromatographic materials and chemicals, except the sample.

False positives are most frequently caused by the inadvertant formation during the sample collection, work-up or analysis of precisely those materials which one is analyzing for. If a N-nitroso compound is found to be present in an entirely new sample, serious consideration must be given to the possibility of a false positive. For example, Angeles, R.M. et al (1978), have recently described the artifactual formation of various N-nitrosamines during extraction of environmental samples. They have shown that inorganic nitrite is solid phase can serve as a nitrosating agent for solutions of organic amines in non-aqueous solvents (CH_2Cl_2, CH_2ClBr, CH_2Br_2, etc.). Logsdon, D.J. et al (1977) have also recently reported on the artifactual formation of N-nitrosamines during the analysis of water samples for organic matter.

A simple precaution to minimize the possibility of artifact formation is to use the bare minimum of analytical steps. This approach is feasible with the GC-TEA and HPLC-TEA methods of N-nitroso analysis, provided that the sample(s) are in a form suitable for direct introduction into the apparatus. For example, Ross,R. et al (1977) have directly introduced aqueous pesticide formulations into both GC-TEA and HPLC-TEA in order to show that NDMA was present in the formulation itself. In the case of cutting fluids, Fan, T.Y. et al (1977b) introduced crude formulations of up to 40% triethanolamine and 18% sodium nitrite directly into HPLC-TEA in order to confirm the presence of NDElA.

If a particular sample cannot be introducted directly into the TEA, it should be extracted and worked up with as few analytical operations as possible. In the case of air samples, Fine, D.H. et al (1977) were able to directly analyze by GC-TEA, materials isolated using cryogenic trapping, without any extraction or concentration. Thus, the possibility of artifactual formation was limited to method of sampling and/or the chromatographic or detector conditions employed.

The source of the nitrosating agent which could be responsible for a positive artifact has included nitrite contamination of the sample itself (Fan, T.Y. et al, 1977; Fine, D.H., 1978), open column chromatography on nitrite contaminated packing materials for GC and LC columns (Eisenbrand, G. and Spiegelhalder, B., 1977), use of too high an injection port temperature in GC analysis of a complex sample (Fan, T.Y. and Fine, D.H., 1978), absorption of nitrogen oxides from ambient air (Eisenbrand, G. et al, in press), N-nitrosamine contaminated deionized water (Gough, T.A. et al, 1977; Fiddler, W. et al, 1977) and organic solvents (Eisenbrand, G. et al, 1978). The most frequent source of the amine precursors is the sample itself. In order to determine if all or part of the N-nitroso compounds present are a result of the analytical methods, a number of experiments are arranged so that they yield maximum information with a minimum of time and effort.

The first such experiment is the addition of readily nitrosatable amine, together with a nitrosating agent (inorganic nitrite and/or oxides of nitrogen) to the original sample. Usually, there are several possible candidates for the amine precursor and nitrosation agent. This is then followed by the same sequence of analytical steps as for the analysis itself. If there is an increase found in the amount of N-nitroso compound(s) present, then artifact formation may have occurred. Two additional precursor control experiments then become necessary. Excess amine(s) is then added to the sample, without any added nitrosating agent, and the amount of N-nitroso derivative determined. If additional N-nitroso compounds are observed, then it is likely that artifact formation has occurred. If no increased formation of N-nitroso material is observed, then a third experiment is carried out with added nitrosating agent alone, in the absence of added amine(s). If additional N-nitroso compounds are not formed, then it can be reasonably assumed that there was no artifact formation in the original analysis. If, on the other hand, enhancement is observed, then artifact formation may have occurred. If artifact formation has indeed occurred, then the analytical method must be modified to avoid this.

In order to reduce the number of precursor experiments required, initial work should be done with rather high concentrations of amine(s) and nitrosating agent or amine (nitrosating agent) alone. The amounts of precursors added to the sample in these initial experiments should be from 10 to 100 times the amount of N-nitroso compound determined originally. If, with these large concentrations, enhancement is not observed, then there is no need to use lower precursor concentrations. However, if high concentrations lead to enhancement, further experiments are needed to progressively lower concentrations.

In the case of air monitoring and crankcase emission sampling, where nitrogen oxides are always present, collection of samples in unsuitable traps creates additional routes for artifact formation of N-nitroso compounds (Challis, B.C. et al, 1978). Validation procedures for air sampling have been described (Fine, D.H. et al, 1977). If the addition of the precursor amine does not lead to enhancement, then positive artifact formation of the N-nitroso compound is probably absent. The use of deuterated amine precursors has been used to resolve the question of artifact formation in air sampling (Fine, D.H. et al, 1977).

USE OF ADDED INHIBITORS

Several workers routinely add nitrosation inhibitors such as ascorbate (Hecht, S.S. et al, 1974), or sulfamic acid (Fan, T.Y. et al, 1977a) to all samples prior to analysis. Nitrosation inhibitors are effective, because at the proper pH they compete with amines for available nitrite (Mirvish, S.S., 1975a; Mirvish, S.S., 1975b). Care is required to ensure that the inhibitor is added in excess so as to account for the available nitrite. If addition of an inhibitor decreases the amount of N-nitroso compound which is observed, it is probable that some or all of the N-nitroso material originally determined was due to artifact formation.

ARTIFACT FORMATION VIA TRANSNITROSATION

Artifact fornation due to transnitrosation within the sample can be detected by use of control experiments similar to those already discussed. Also, the use of combined GC-TEA and HPLC-TEA can usually eliminate the possibility of artifact formation due to transnitrosation, if this occurs during the chromatographic process itself (Fan, T.Y. and Fine, D.H., 1978). Often a temperature above ambient is required to produce a significant transnitrosation. Thus, by working room temperature, as is done with most HPLC, this problem can usually be entirely prevented.

False positives are known in gas chromatography (Fan, T.Y. and Fine, D.H., 1978; Umbreit, G.R., 1977) and to a lesser extent in HPLC (Eisenbrand, G. and Spiegelhalder, B., 1977; Freed, O.J. and Mujsce, A.M., 1977). The formation of a N-nitroso material on-column during HPLC on nitrite-free packing is unlikely. If a N-nitroso material is shown to be present using a variety of HPLC columns and conditions, it is strongly indicative that no positive artifact formation has occurred during HPLC. For volatile N-nitrosamines, a combination of GC and HPLC techniques has been used to eliminate positive artifact formation during chromatograph (Ross, R. et al, 1977; Fine, D.H. et al, 1977; Fan, T.Y. and Fine, D.H., 1978).

Appendix K

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